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(54) POROUS HONEYCOMB STRUCTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous honeycomb structure which can effectively achieve an improvement in the efficiency of catching and storing soot or the like, the reduction of pressure drop, an improvement in the cleaning performance by the effective utilization of a catalyst and prolonging of the time for catching and storing the soot or the like and can eventually improve the elution threshold and isotatic strength during the regeneration of a filter.

SOLUTION: The porous honeycomb structure which is provided with the partitions of porous ceramics consisting essentially of cordierite, having 55 to 75% of porosities and 15 to 35 μm of mean pore diameter and having a pore distribution expressed by $\text{Lr} > 0.3 \times \text{P}/100 + 0.91$ (1) is provided. In the expression, Lr signifies a mean ratio of development lengths and P signifies the porosities obtained from a total pore volume when the total pore volume is measured by a mercury pressed into type porosimeter and the true specific gravity of the cordierite is determined as 2.52 g/cc.

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CLAIMS

[Claim(s)]

[Claim 1]

It is a porosity honeycomb structure object equipped with two or more septa which use cordierite as a principal component and consist of porous ceramics with a% [of porosity] of 55 - 75, and an average pore diameter of 15-35 micrometers,

The porosity honeycomb structure object with which pore of this septum is characterized by having the pore distribution shown in the following conditional expression (1).

[Equation 1]

$$L_r > 0.3 \times P / 100 + 0.91 \quad (1)$$

"Lr means the average length-of-developed-blank ratio called for with the following formula (2) among the above-mentioned conditional expression (1). moreover, when P measures the total pore volume by the mercury pressure close type porosimeter and carries out true specific gravity of cordierite in 2.52g/cc, it means the porosity called for from the total pore volume concerned. **

[Equation 2]

$$L_r = L_o / 4 \quad (2)$$

"Lo means the average length of developed blank (average of the die length which included the front face of the pore which carried out opening in the septum front face) for which carried out 4mm (straight-line die length which disregarded the existence of pore which carried out opening to septum front face) sensing pin, and it asked along the septum front face about ten places of the arbitration on the front face of a septum among the above-mentioned formula (2) using a surface roughness measurement machine, and Lr means an average length-of-developed-blank ratio."

[Claim 2]

The porosity honeycomb structure object according to claim 1 with which the pore of said septum has the fault pore distribution shown in the following conditional expression (3) in the septum thickness direction.

[Equation 3]

$$X < -33 \times P / 100 + 28 \quad (3)$$

"X is the average of the primary component magnitude spectrum (F) called for from the following formula (4) and (5), and a secondary component magnitude spectrum (S) among the above-mentioned conditional expression (3). Moreover, when P measures the total pore volume by the mercury pressure close type porosimeter and carries out true specific gravity of cordierite in 2.52g/cc, it means the porosity called for from the total pore volume concerned. "

[Equation 4]

$$F = \sqrt{X_{SR}(1)^2 + X_{SI}(1)^2} \quad (4)$$

"F expresses the primary component magnitude spectrum at the time of being referred to as k= 1 in the following transformation (6) among the above-mentioned formula (4). Moreover, XSRe (1) and XSIm (1) show the real part and imaginary part at the time of being referred to as k= 1 in the following transformation (6), respectively. "

[Equation 5]

$$S = \sqrt{X_{SR}(2)^2 + X_{SI}(2)^2} \quad (5)$$

"S expresses the secondary component magnitude spectrum at the time of being referred to as k= 2 in the following transformation (6) among the above-mentioned formula (5). Moreover, XSRe (2) and XSIm (2) show the real part and imaginary part at the time of being referred to as k= 2 in the following transformation (6), respectively. "

[Equation 6]

$$X_s(k) = \sum_{n=0}^{255} x(n) \left(\cos \frac{2\pi k}{256} \cdot n - j \sin \frac{2\pi k}{256} \cdot n \right) \quad (6)$$

"Among the above-mentioned transformation (6), XS (k) expresses discrete Fourier transform and k expresses a degree. Moreover, n is the integer of 0-255 and expresses the division location at the time of dividing a septum cross section into 256 in order in the thickness direction from the septum outermost surface section (n= 0). Moreover, X (n) expresses the rate of surface ratio which a pore part occupies in the septum cross-section field to division location n-n +1. "

[Claim 3]

The porosity honeycomb structure object according to claim 1 or 2 said whose septum is the thickness of 350 micrometers or less.

[Claim 4]

A porosity honeycomb structure object given in any 1 term of claims 1-3 whose coefficients of thermal expansion in 40-800 degrees C are less than [1.0x10-6/degree C].

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to a porosity honeycomb structure object and its manufacture approach. By controlling pore distribution of a septum, in more detail Protraction of uptake time amount, Can attain effectively the improvement in collection efficiency, and reduction of pressure loss, as a result [in which the prevention of an erosion and the improvement in AISO static reinforcement at the time of filter playback are possible] While being able to attain effectively improvement in the purification engine performance, and reduction of pressure loss in the filter for emission gas purification, and a list, it is related with the porosity honeycomb structure object which makes the catalyst support which is excellent in AISO static reinforcement, and can be applied.

[0002]

[Description of the Prior Art] A close-up of the effect of the environment on car motor, the particulate matter especially discharged from a diesel power plant etc., or NOx is taken greatly recently, and use of a porosity honeycomb structure object is variously considered as an important means to remove such harmful matter.

[0003] For example, in the honeycomb structure object which has two or more through tubes divided by the porous septum, uptake and the honeycomb filter to remove are developed in the particulate matter in exhaust gas by making exhaust gas flow into each through tube which makes the structure which ******(ed) in a mutually different location in respect of the both ends which a through tube punctures, and carries out opening to the end face of 1, and passing the septum of the honeycomb structure inside of the body compulsorily. Moreover, development is furthered also for the catalyst object of the honeycomb structure which made the catalyst which decomposes all septa as a new attempt which raises the purification engine performance, and decomposes HC and NOx as a porous body of high porosity support by increasing the amount of catalyst support.

[0004] By the way, if it is in the porosity honeycomb structure object concerned, naturally for the application as a filter, high collection efficiency can be searched for. Moreover, if the soot more than fixed accumulates on the pore which carries out opening to a septum front face, since pressure loss increases rapidly, the playback process which it burns [process] at an elevated temperature and makes a soot usually burned down after fixed time amount use will be performed, but since degradation of a porosity honeycomb structure object will be promoted if this playback process is performed by high frequency, lengthening uptake time amount and reducing the count of a playback process is called for.

[0005] Furthermore, since a porosity honeycomb structure object is extremely put to elevated-temperature-ization at the time of filter playback, in order to prevent the erosion of the septum by the filter playback concerned for the application as a filter, it is desirable to have the heat capacity more than fixed about the whole filter, and in case a soot is burned and the filter concerned is reproduced, it is desired for the maximum amount of soots (the amount of soot marginal playbacks) which does not cause the erosion of a septum to be large.

[0006] On the other hand, for the application as catalyst support, in order to raise the emission-gas-purification engine performance more in recent years, it is requested that the amount of catalyst support should be increased and the attempt which supports a catalyst on the honeycomb structure object formed into high porosity is performed.

[0007] Moreover, also in which application, if it is in the porosity honeycomb structure object with which the request of low-fuel-consumption-izing and a high increase in power is installed in combustion engines, such as a strong diesel power plant, reduction-ization of pressure loss is called for. Furthermore, since a porosity honeycomb structure object is installed near the engine which receives a big vibration continuously, it is necessary to grasp it firmly in metal casing, and also in which application, high AISO static reinforcement is required about the whole honeycomb structure object again.

[0008] The honeycomb structure object which controlled pore distribution of a septum in various range is indicated in order to accept such a request conventionally.

[0009] For example, the honeycomb structure object which controlled the specific surface area (Mm^2/g) of the pore which carries out opening to the patent reference 1 on a septum front face, and the surface roughness ($Nmum$) in the filter front face to $1000M+85N>=530$ is indicated.

[0010] However, this honeycomb structure object is manufactured using the ceramic raw material which controlled the particle size of ceramic raw materials, such as a silica and talc, and porosity was about 60% at the maximum (patent reference 1).

[0011] Moreover, this honeycomb structure object was not what does not take into consideration at all and may fully satisfy requests, such as protraction of uptake time amount, improvement in collection efficiency, improvement in the purification engine performance, and reduction of pressure loss, about distribution of the pore in the interior of septa other than the ratio of the pore which carries out opening to the porosity and septum front face of the whole septum.

[0012] On the other hand, the cordierite honeycomb structure object (patent reference 2) which made the number of 5-40-micrometer stomata five to 40 times for the pore on the front face of a septum to the 40-100-micrometer osculum using the raw material which added an organic blowing agent and carbon as an ostomy agent at the cordierite-ized raw material is proposed.

[0013] However, it was not what also takes this honeycomb structure object into consideration in any way about the ratio of the pore which carries out opening to the septum front face to the porosity of the whole septum. Moreover, with this honeycomb structure object, it was manufactured as ostomy material using the organic blowing agent which is a dense particle and is hollow-ized with heating at first. For this reason, there are few organic blowing agents which carry out opening to a septum front face immediately after extrusion molding, and when a binder gels with heat by a subsequent desiccation process etc. and the Plastic solid hardened, as for the present condition, there was little pore which it will not result by the time even the thing 100 degrees C or less to which it foams at low temperature comparatively expands so greatly that a septum front face is broken through, but carries out opening to a septum front face. Consequently, it was not what has a bias in the pore distribution in the thickness direction of a septum, and may fully be satisfied with this honeycomb structure object of requests, such as improvement in collection efficiency, protraction of uptake time amount, and reduction of pressure loss. Moreover, it hurt very much according to the bias of this pore distribution, and purification engine performance in which the rate of a deployment which actually contributes to a purification reaction was small, and sufficient was not obtained. Furthermore, that such a problem should be solved, when further high porosity-ization of the whole septum was attained, there was a problem of producing the erosion of the local septum at the time of the filter playback by a fall and heat-capacity fall of AISO static reinforcement.

[0014] moreover, also with the honeycomb structure object manufactured using the ostomy agent of non-foaming systems, such as PMMA and PET Like the above, there is little present condition and the pore which carries out opening to a septum front face is not what may fully satisfy requests, such as improvement in collection efficiency, protraction of uptake time amount, improvement in the purification engine performance, and reduction of pressure loss, effectively. When further high porosity-ization of the whole septum was attained, there was a problem of producing the erosion of the local septum at the time of the filter playback by a fall and heat-capacity fall of AISO static reinforcement.

[0015]

[Patent reference 1]

The patent No. 2726616 official report

[Patent reference 2]

JP,9-77573,A

[0016]

[Problem(s) to be Solved by the Invention] This invention aims at offering the porosity honeycomb structure object which can be made in view of an above-mentioned problem, and can attain effectively improvement in collection efficiency, such as a soot, improvement in the purification engine performance by deployment of a catalyst, reduction of pressure loss, and protraction of uptake time amount, as a result can improve the erosion limitation and AISO static reinforcement at the time of filter playback.

[0017]

[Means for Solving the Problem] When this invention person manufactures a honeycomb structure object using the plastic matter which added foaming resin [finishing / foaming] as a result of inquiring wholeheartedly in order to solve an above-mentioned technical problem, he is high porosity. And much pores which carry out opening were formed in the septum front face, the honeycomb structure object of pore distribution with which a septum length-of-developed-blank ratio becomes beyond a specific value to the whole porosity was acquired, according to the honeycomb structure object concerned, it resulted in the knowledge that the conventional technical problem mentioned above can be solved, and this invention was completed.

[0018] namely, a honeycomb structure object equipped with two or more septa which according to this invention use cordierite as a principal component and consist of porous ceramics with a% [of porosity] of 55 - 75, and an average pore diameter of 15-35 micrometers -- it is -- the pore of the septum concerned -- the following conditional expression (1) -- (-- it may only be hereafter called "conditional expression (1)") -- the porosity honeycomb structure object characterized by having the shown pore distribution is offered.

[0019]

[Equation 7]

$$Lr > 0.3 \times P / 100 + 0.91 \quad (1)$$

[0020] "-- Lr means the average length-of-developed-blank ratio called for by the following formula (2) and (it only being hereafter called "formula (2)") among the above-mentioned conditional expression (1). Moreover, when P measures the total pore volume by the mercury pressure close type porosimeter and carries out true specific gravity of cordierite in 2.52g/cc, it means the porosity called for from the total pore volume concerned. "

[0021]

[Equation 8]

$$Lr = L_o / 4 \quad (2)$$

[0022] "Lo means the average length of developed blank (average of the die length which included the front face of the pore which carried out opening in the septum front face) for which carried out 4mm (straight-line die length which disregarded the existence of pore which carried out opening to septum front face) sensing pin, and it asked along the septum front face about ten places of the arbitration on the front face of a septum among the above-mentioned formula (2) using a surface roughness measurement machine, and Lr means an average length-of-developed-blank ratio."

[0023] moreover, this invention -- setting -- further -- the pore of the septum concerned -- the septum thickness direction -- the following conditional expression (3) -- (-- it may only be hereafter called "conditional expression (3)") -- what has the shown fault pore distribution is desirable.

[0024]

[Equation 9]

$$X < -33 \times P / 100 + 28 \quad (3)$$

[0025] "-- X is the average of the primary component magnitude spectrum (F) called for from the following formula (4) and (5), and (it being hereafter called "formula (4)" and "formula (5)", respectively), and a secondary component magnitude spectrum (S) among the above-mentioned conditional expression (3). Moreover, P means the porosity called for like the case of said conditional expression (1). "

[0026]

[Equation 10]

$$F = \sqrt{X_{SR\alpha}(1)^2 + X_{SI\alpha}(1)^2} \quad (4)$$

[0027] "F expresses the primary component magnitude spectrum at the time of being referred to as k= 1 in the following transformation (6) among the above-mentioned formula (4). Moreover, XSRe (1) and XSIm (1) show the real part and imaginary part at the time of being referred to as k= 1 in the following transformation (6), respectively. "

[0028]

[Equation 11]

$$S = \sqrt{X_{SR\alpha}(2)^2 + X_{SI\alpha}(2)^2} \quad (5)$$

[0029] "S expresses the secondary component magnitude spectrum at the time of being referred to as k= 2 in the following transformation (6) among the above-mentioned formula (5). Moreover, XSRe (2) and XSIm (2) show the real part and imaginary part at the time of being referred to as k= 2 in the following transformation (6), respectively. "

[0030]

[Equation 12]

$$X_s(k) = \sum_{n=0}^{255} x(n) \left(\cos \frac{2\pi k}{256} \cdot n - j \sin \frac{2\pi k}{256} \cdot n \right) \quad (6)$$

[0031] "Among the above-mentioned transformation (6), XS (k) expresses discrete Fourier transform and k expresses a degree. Moreover, n is the integer of 0-255 and expresses the division location at the time of dividing a septum cross section into 256 in order in the thickness direction from the septum outermost surface section (n= 0). Moreover, X (n) expresses the rate of surface ratio which a pore part occupies in the septum cross-section field to division location n-n +1. "

[0032] In this invention, it is desirable to set thickness of a septum to 350 micrometers or less. Moreover, the coefficient of thermal expansion in 40-800 degrees C can be made into less than [1.0x10-6/degree C] about the whole honeycomb structure object.

[0033]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained concretely.

[0034] The porosity honeycomb structure object of this invention uses cordierite as a principal component, has the pore of specific porosity and an average pore diameter, and has the porosity distribution with which the length-of-developed-blank ratio and porosity on each front face of a septum fill specific conditional expression further. Hereafter, it explains concretely.

[0035] In this invention, any, such as orientation, non-orientation, alpha crystalline substance, and beta crystalline substance, are sufficient as the principal component slack cordierite of a septum. Moreover, you may be independent one sort or the thing contained two or more sorts as components other than cordierite about a mullite, zircon, aluminum titanate, clay bond silicon carbide, a zirconia, a spinel, an indialite, Safi Lynn, corundum, or a titania.

[0036] Moreover, in this invention, the septum of a honeycomb structure object consists of high porosity ceramics of 65 - 75% of porosity more preferably 55 - 75% of porosity.

[0037] Since the transparency resistance to exhaust gas [in / that porosity is less than 55% / a septum] is too strong, even if it controls pore distribution to mention later, it becomes difficult to reduce pressure loss to extent which is convenient practically. Moreover, it also becomes difficult to obtain desired catalyst *****. On the other hand, if porosity exceeds 75%, AISI static

reinforcement will become low and it will become easy to produce breakage in the case of grasping to a case.

[0038] Moreover, in this invention, the pore which exists in the septum of these porous ceramics is a thing with an average pore diameter of 15-35 micrometers.

[0039] Although collection efficiency becomes it high that an average pore diameter is less than 15 micrometers, initial pressure loss becomes large. On the other hand, if an average pore diameter exceeds 35 micrometers, even if it controls pore distribution like the after-mentioned, it will become difficult to secure the collection efficiency demanded practically. Moreover, it is easy to deposit a soot on the interior of a septum, in case it is regeneration, a soot is cinder-easy and accumulates in the interior of a septum, and even if it is after regeneration, a soot deposition pressure loss may not become low.

[0040] The honeycomb structure object of this invention has further the pore distribution from which the length-of-developed-blank ratio on each front face of a septum becomes beyond a specific numeric value to the porosity of the whole septum, and the pore distribution with which the conditions of said conditional expression (1) are specifically filled.

[0041] Thereby, among [all] pore, since the useful soot deposition permission volume becomes large substantially, collection efficiency can be improved effectively and uptake time amount can be lengthened. Moreover, since the septum front face to the porosity of the whole septum has many rates of the pore which carries out opening, pressure loss can be reduced effectively or the purification engine performance can be effectively improved according to increase of the amount of catalyst support, or the supported increase of the rate of a deployment of a catalyst. Moreover, even if it makes the porosity of the whole septum low to some extent so that clearly from the above thing, it is possible about collection efficiency, uptake time amount, the purification engine performance, and pressure loss to acquire sufficient property, as a result AIS0 static reinforcement and the amount of soot marginal playbacks can be increased.

[0042] the septum in the porosity honeycomb structure object of this invention have still more desirable fault pore distribution of the thickness direction at the point what have the pore distribution show in said conditional expression (3) can raise synthetically further many properties for which the honeycomb structure object of the septum erosion, the AIS0 static reinforcement, the collection efficiency, the purification engine performance, pressure loss, and uptake time amount at the time of filter playback be ask.

[0043] That is, the honeycomb structure object which fulfills the conditions of said conditional expression (3) is distributed over homogeneity, without the pore in which fluctuation of fault porosity distribution is small and a septum exists being unevenly distributed in the interior of a septum, therefore a soot hardly deposits it on the interior of a septum, but since there are also few amounts of soots which remain after filter playback, it can make a soot deposition pressure loss still smaller. Moreover, improvement in collection efficiency, protraction of uptake time amount, and reduction of pressure loss can be attained more with a high level, satisfying these properties, in order that the honeycomb structure object which fulfills the conditions of said conditional expression (3) may cause neither the fall of AIS0 static reinforcement, nor the fall of the amount of soot marginal playbacks by reduction in heat capacity locally in each part of a septum. The higher purification engine performance can be attained satisfying AIS0 static reinforcement similarly, since the amount of catalyst support and the supported rate of a deployment of a catalyst are increased further.

[0044] Here, the fault porosity distribution in the septum thickness direction shown in said transformation (6) can be measured with a scanning electron microscope (SEM). First, the septum cross section of a honeycomb structure object is observed by one 100 times the scale factor of this, and the image data is specifically binary--ization-processed with image-analysis software, and let the black section as a pore part and let the white section be a honeycomb base material part. And as shown in drawing 1 , it computes and asks for the ratio of the area in which a cross section is divided into 256 in the septum thickness direction, and a pore part occupies it for each [which was divided] tomographic-layer field of every in the septum die-length direction by width of face of 1mm. The result of having carried out the Fourier transform of the fault porosity distribution $X(n)$ which shows an example of the fault porosity distribution $X(n)$ for which carried out in this way and drawing 2 was asked to drawing 3 at drawing 2 by each series is shown.

[0045] What is necessary is for there to be especially no limit about points other than [, such as septum thickness of a honeycomb structure object, a cel configuration, and a cel pitch,] the various conditions of the pore which a septum has, and just to consider as a suitable design in this invention, according to an application etc. But in order to give a desired filter function, it is desirable to consider as the structure which ******(ed) two or more through tubes which carry out opening to an emission close side edge side and an exhaust gas discharge side edge side in a location which is mutually different in respect of both ends.

[0046] Moreover, a catalyst can be supported to the septum of the porosity of a honeycomb structure object, and it can consider as a catalyst object. When using as catalyst support, as for the thickness of 6 - 1500 cel / inch 2 (0.9 - 233 cel / cm²), and a septum, it is [a cel consistency] desirable to consider as the range of 50-2000 micrometers (about two to 79 mil). Moreover, the shaft-orientations (exhaust gas flow direction) die length in the case of using as catalyst support is usually 100-250mm preferably 60-300mm.

[0047] Moreover, an adsorption layer may be prepared in catalyst support and the alumina which has high specific surface area, and the thing which uses a zeolite as a principal component are usually suitably used for it. Although any of a natural article and synthetic compounds are sufficient as a zeolite and especially a class is not limited, it is thermal resistance, endurance, and a hydrophobic point, and 40 or more things are suitably used for a Si/aluminum ratio. Specifically, ZSM-5, USY, beta-zeolite, Silicalite, metallasilicate, etc. can use it suitably.

[0048] Moreover, a honeycomb structure object may be made to support a catalyst component directly, and an adsorption layer may be made to support it.

[0049] In this invention, since the reduction in porosity is also possible to some extent as uniform pore distribution was had and mentioned above about the whole septum, even if it makes a septum thinner, the erosion of a septum can be prevented, and desired AISO static reinforcement can be secured. Therefore, pressure loss can use septum thickness as a porosity honeycomb structure object with the high rate of a catalyst deployment smaller by being referred to as 350 micrometers or less.

[0050] Moreover, the coefficient of thermal expansion in 40-800 degrees C can make the honeycomb structure object of this invention less than [1.0x10⁻⁶/degree C] by using the foaming resin [finishing / foaming] which does not check a cordierite-ized reaction as a means to form the pore near a septum front face, and it can raise the thermal shock resistance at the time of elevated-temperature use.

[0051] In this invention, the method of manufacturing the foaming resin [finishing / foaming] of an acrylic microcapsule etc. as an ostomy agent in a cordierite-ized raw material as an approach of considering as the pore distribution mentioned above using the plastic matter added and kneaded is desirable.

[0052] If the plastic matter which added foaming resin [finishing / foaming in the air] from the beginning is used, since the foaming resin [finishing / foaming] released from thrust immediately after extrusion molding of the plastic matter concerned will expand within a septum, what exists near the septum front face will be protruded from a septum front face, and will expand, and much pores which the outer wall finally explodes and carry out opening to a septum front face will be formed. Moreover, in the condition before desiccation, since it is in the same condition when much pores are already formed, even if a honeycomb Plastic solid hardens by gelation of a binder at a subsequent desiccation process etc., the number of the pores which carry out opening to a septum front face does not decrease by it.

[0053] But in this invention, particle size can be controlled about ceramic raw materials, such as talc and a silica, and the approach of controlling the porosity and average pore diameter of a filter which are obtained can also be combined. However, since considering as desired pore distribution becomes difficult even if it uses foaming resin [finishing / foaming] together when the particle size to be used is too large, if it is talc and is a thing with a particle size of 50 micrometers or less and a silica, it is desirable to use a thing with a particle size of 100 micrometers or less.

[0054] Moreover, it may set to this invention and other ingredients, such as carbon, wheat flour, starch, phenol resin, a polymethyl methacrylate, polyethylene, or polyethylene terephthalate, may be made to contain as an ostomy agent. Since it burns in a different temperature region from the temperature region which a binder and foaming resin carry out oxidative degradation of the carbon,

such as graphite, especially, and causes generation of heat, it is desirable at the point of being hard to generate a baking piece.

[0055] Moreover, when using foaming resin [finishing / foaming] independently as an ostomy agent, it is desirable to carry out 0.5-5 mass section content of the foaming resin [finishing / foaming / to the cordierite-ized raw material 100 mass section], and it is more desirable to carry out 1-3.5 mass section content.

[0056] The pressure loss of the honeycomb structure object with which porosity can become that the content of foaming resin [finishing / foaming] is under the 0.5 mass section with less than 55% becomes large. On the other hand, if the content of foaming resin [finishing / foaming] exceeds 5 mass sections, porosity becomes larger than 75%, and the AISO static reinforcement and the heat capacity of a honeycomb structure object which are obtained will fall, and it will become intolerable at practical use.

[0057] Furthermore, when using together carbon, such as graphite, and foaming resin [finishing / foaming], it is more desirable to carry out 1-3 weight section content of the foaming resin [finishing / 5 - 15 weight section and foaming to carbon / it is desirable to carry out 0.5-3 weight section content of the foaming resin / finishing / 5 - 25 weight section and foaming to carbon /, and] from the same point to the cordierite-ized raw material 100 weight section.

[0058] In this invention, it is usually desirable as other additives to make dispersants, such as binders, such as hydroxypropyl methylcellulose, methyl cellulose, hydroxyethyl cellulose, carboxyl methyl cellulose, or polyvinyl alcohol, or ethylene glycol, a dextrin, fatty-acid soap, and polyalcohol, etc. contain. In addition, in this invention, even if a Plastic solid hardens by gelation of the binder in a desiccation process, it is as having mentioned above that the bias of pore distribution does not arise.

[0059]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples at all. In addition, the approach shown below about the honeycomb structure object acquired in each example and each example of a comparison estimated.

[0060]

1. Evaluation Approach

(1) The average aperture of pore

It measured by the mercury pressure close type porosimeter by the microphone ROMERI tex company.

[0061]

(2) Porosity

The total pore volume was measured by the mercury pressure close type porosimeter by the microphone ROMERI tex company, true specific gravity of cordierite was carried out in 2.52g/cc, and porosity was calculated from the total pore volume concerned.

[0062]

(3) Average length-of-developed-blank ratio

On ten septum front faces chosen as arbitration using the FTS-S4C mold surface roughness measurement machine made from Taylor HOBUSON The sensing-pin tip of 2micromR was contacted 4mm along the septum front face by the straight-line die length on the front face of a septum (die length which disregarded the existence of pore which carried out opening), and the length of developed blank (die length in consideration of the inside of the pore which carried out opening) corresponding to the straight-line die length concerned was measured. Subsequently, the average (Lo) of the length of developed blank in ten septum front faces was calculated, and this average length of developed blank (Lo) was **(ed) by 4 of straight-line die length, and it asked for the average length-of-developed-blank ratio (Lr). Moreover, it **(ed) and asked for the average length-of-developed-blank ratio per unit porosity with the porosity of the whole septum which asked for this average length-of-developed-blank ratio by the approach mentioned above.

[0063]

(4) Homogeneity of fault porosity (average of a primary component magnitude spectrum (S) and a secondary component magnitude spectrum (F) (X))

As shown in drawing 1 , the septum cross section of a honeycomb structure object was photoed by

SEM in 1mm in the septum die-length direction, the image data was binary--ization-processed with image-analysis software, the black section was used as the pore part and the white section was used as the honeycomb base material part. Then, the 300-micrometer septum was divided in the thickness direction 256, and the rate of surface ratio of the pore part in each divided field ($n-n+1$) was computed sequentially from the septum front face, as shown in drawing 2. subsequently, change of the rate of surface ratio of the pore part in the septum thickness direction -- a Fourier analysis -- carrying out -- frequency (n) = -- it asked for each wave amplitude spectrum as a wave of 1 and 2, and considered as the primary component magnitude spectrum (S) and the secondary component magnitude spectrum (F), respectively. Finally, the average (X) of these numeric values was calculated and the homogeneity of fault porosity was evaluated.

[0064]

(5) Collection efficiency

The honeycomb structure object acquired in each example and the example of a comparison was made to carry out fixed time amount (2 minutes) passage of the exhaust gas made to generate a soot with a soot generator, uptake of the soot contained in after [filtering] exhaust gas was carried out through the filter paper, and the weight (W_1) of a soot was measured. Moreover, uptake of the exhaust gas made to generate the same time amount and a soot was carried out through the filter paper, without passing a filter, and the weight (W_2) of a soot was measured. Subsequently, it substituted for the formula (7) showing each obtained weight (W_1) (W_2) below, and collection efficiency was searched for.

[0065]

[Equation 13]

$$(W_2 - W_1) / (W_2) \times 100 \quad (7)$$

[0066]

(6) Soot uptake pressure loss

First, the pressure welding of the bore phi130mm ring is carried out, the soot which made it generate with a soot generator was flowed within the limits of phi130mm of a honeycomb structure object through this ring, and the both-ends side of the honeycomb structure object acquired in each example and the example of a comparison was made to carry out uptake of the 10g soot. Subsequently, after the honeycomb structure object had carried out uptake of the soot, the differential pressure before and behind a sink and a filter was measured for the air of 2.27Nm³/min, and the pressure loss in the condition of having carried out uptake of the soot was evaluated.

[0067]

(7) Emission-gas-purification effectiveness

Canning of the catalyst object which supported the catalyst on the honeycomb structure object acquired in each example and the example of a comparison was carried out to the metal case, and the purification effectiveness of HC was evaluated using the 5l. diesel power plant. HC concentration B-2 in the HC concentration B1 in a sink and the exhaust gas before introducing into a catalyst object and the exhaust gas after catalyst object passage was measured for the exhaust gas from an engine on the catalyst object of honeycomb structure, and emission-gas-purification effectiveness was searched for by $100 \times (B_1 - B_2) / B_1$ formula of B1.

[0068]

2. It is as a result of Evaluation to Example and Example of Comparison, and List.

(Example 1)

Talc [of the mean particle diameter shown in Table 1 and particle size distribution] B (mean particle diameter: 45 micrometers), kaolin (10 micrometers), alumina (mean particle diameter: 5 micrometers), aluminum-hydroxide (mean particle diameter: 3 micrometers), and fused silica B (mean particle diameter: 40 micrometers) was mixed at a rate of talc B40 mass %, kaolin 20 mass %, alumina 14 mass %, aluminum-hydroxide 16 mass %, and fused silica B10 mass %, as shown in Table 2, and the cordierite-ized raw material was prepared.

[0069] Subsequently, as shown in Table 2, to this cordierite-ized raw material 100 mass section, 2 mass sections, the hydroxypropyl-methylcellulose 4 mass section, the lauric-acid potash soap 0.5 mass section, and the water 30 mass section were supplied and kneaded, the foaming resin [finishing / foaming] which consists of an acrylonitrile-methyl methacrylate copolymer was made

into plasticity, and the cylinder-like plastic matter was fabricated with the vacuum kneading machine, and this reversible raw material was fed into the extrusion-molding machine, and was fabricated in the shape of a honeycomb.

[0070] Subsequently, the bone dry of the acquired Plastic solid was carried out by hot air drying after dielectric drying, and the both-ends side was cut in the predetermined dimension.

[0071] Subsequently, the through tube ***** (ed) alternately the through tube in the desiccation object of the shape of this honeycomb in respect of the both ends which carry out opening by the slurry which consists of a cordierite-ized raw material of the same presentation.

[0072] Finally, it calcinated and 1420 degrees C (honeycomb filter) of honeycomb structure objects of size:phi144 mmxL152mm, septum thickness:300micrometer, and number of cels:300 cel / inch² were acquired for 4 hours.

[0073]

(Examples 2-10 and examples 1-8 of a comparison)

In the example 1, the honeycomb structure object (honeycomb filter) was acquired like the example 1 except having used the cordierite-ized raw material and ostomy agent of the presentation shown in Table 1 and 2.

[0074]

(Evaluation result)

With the honeycomb structure object of the examples 1-10 which carried out 2-3.5 mass section addition of the foaming resin [finishing / foaming / as an ostomy agent as shown in Tables 2 and 3], the average pore diameter of a septum was 16.0-34.6 micrometers, and porosity was 55.5 - 72.0%. Moreover, pore distribution of the acquired honeycomb structure object was filling said conditional expression (1) and the conditions of (3) with any example, as shown in drawing 4 and 5. Moreover, the conditions of these relational expression are filled also with the honeycomb structure object of examples 1 and 7 using comparatively coarse talc and a silica raw material, and it guessed for foaming resin [finishing / foaming] to expand within a septum immediately after shaping.

[0075] on the other hand, example of comparison 1- manufactured using graphite, and PET and PMMA as an ostomy agent -- pore was unevenly distributed in the interior, and as shown in drawing 4 and 5, said conditional expression (1) and neither of the conditions of (3) was filled with 4 or 6 honeycomb structure objects.

[0076] For this reason, when the property of the honeycomb structure object of this porosity was compared, as shown in Table 3, the honeycomb structure object of each example had collection efficiency higher than the honeycomb structure object of each example of a comparison, and the uptake pressure loss was low [compared with the honeycomb structure object which has the comparable porosity of each example of a comparison with the honeycomb structure object of each example, the average (X) of a primary component magnitude spectrum and a secondary component magnitude spectrum was small, and], as shown in drawing 5 . Moreover, through each honeycomb structure object, as shown in drawing 6 , the inclination for a soot uptake pressure loss to become small was accepted, so that the average (X) of a primary component magnitude spectrum and a secondary component magnitude spectrum was small.

[0077] On the other hand, although the conditions of said conditional expression (1) were filled with the honeycomb structure object of the example 5 of a comparison using a very coarse silica raw material since a part of silica particle appeared in the septum front face and it formed pore, an average pore diameter is 35 micrometers or more, and the conditions of said conditional expression (3) were not fulfilled. For this reason, with this honeycomb structure object, collection efficiency became very low with 65%, and the soot uptake pressure loss also became very large.

[0078] Moreover, said conditional expression (1) and neither of the conditions of (3) was filled with the honeycomb structure object of the example 7 of a comparison manufactured using the non-foamed foaming resin to which it foams above 80 degrees C, but since porosity was very as low as 44.4%, the soot uptake pressure loss became very large. The Plastic solid hardened this by gelation of a binder at the desiccation process, and since resin was prevented from foaming expanding [non-foamed] within a Plastic solid, it was considered.

[0079] Moreover, with the honeycomb structure object of the example 8 of a comparison which used together and manufactured the graphite 10 weight section and the foaming resin 3.5 weight section

[finishing / foaming], since porosity became 75% or more and AISO static reinforcement became very small, it was not able to set to the fixture for measurement of a soot uptake pressure loss.

[0080]

[Table 1]

	平均粒径(μm)
タルク A	20
タルク B	45
カオリン	10
アルミナ	5
水酸化アルミニウム	3
溶融シリカ A	25
溶融シリカ B	40
シリカ A	5
シリカ B	130
グラファイト	40
発泡済み発泡樹脂	50
未発泡発泡樹脂	15
PMMA	55
PET	50

[0081]

[Table 2]

	コーティング剤配合割合(重量%)						造孔剤配合割合(重量%)			
	タルク	カオリン	アルミナ	水酸化アルミニウム	シリカ	消泡シリカ	グラファイト	発泡済み発泡樹脂	未発泡樹脂	
実施例 1	B : 40	20	14	16		日 : 10			2	
実施例 2	B : 40	20	14	16		A : 10			2	
実施例 3	B : 40	20	14	16		A : 10	10		2	
実施例 4	B : 40	20	14	16	A : 10		10		2	
実施例 5	B : 40	20	14	16		A : 10		10		
実施例 6	A : 39	19	14.5	16.5	B : 11					2.5
実施例 7	B : 40	20	14	16		A : 10	10			2.5
実施例 8	B : 40	20	14	16		A : 10		10		
実施例 9	B : 40	20	14	16	A : 10			10		3
実施例 10	B : 40	20	14	16	A : 10			10		3
実施例 11	B : 40	20	14	16	A : 10				3.5	
比較例 1	B : 40	20	14	16		B : 10	2			
比較例 2	B : 40	20	14	16		B : 10	15		10	
比較例 3	B : 40	20	14	16		A : 10	20		10	5
比較例 4	B : 40	20	14	16		A : 10	25		15	10
比較例 5	B : 40	20	14	16	B : 10	A : 10	25		25	10
比較例 6	A : 39	19	14.5	16.5	B : 11				10	5
比較例 7	B : 40	20	14	16	B : 10		20		10	5
比較例 8	B : 40	20	14	16	A : 10		20		10	5
比較例 9	B : 40	20	14	16	B : 10			2		
									10	

[0082]
[Table 3]

	気孔率 (%)	気孔径 (μm)	熱膨張係数 ($\times 10^{-4}$ / $^{\circ}\text{C}$)	隔壁表面 長さ比	$L_t \times (0.3 \times \text{気孔率} / 100 + 0.91)$	パワースペックル X-12次平均値 X	$X \times (-33 \times \text{気孔率} / 100 + 28)$	捕集効率 (%)	捕集圧損 (kPa)	接着力強化効率 (%)
実施例 1	55.5	25.4	0.4	1.09	0.01	7.6	-2.1	90	0.8	
実施例 2	55.7	20.4	0.4	1.09	0.01	7.2	-2.4	92	0.5	
実施例 3	59.6	24.6	0.6	1.12	0.03	6.1	-2.2	90	0.9	
実施例 4	60.5	16.0	0.4	1.10	0.01	4.1	-3.9	96	8.1	
実施例 5	59.5	25.2	0.6	1.13	0.04	4.0	-4.4	90	8.0	
実施例 6	59.1	34.6	0.7	1.14	0.05	7.7	-0.8	85	9.4	
実施例 7	65.8	23.1	0.7	1.12	0.01	3.5	-2.8	91	7.1	
実施例 8	65.8	23.9	0.8	1.13	0.02	3.1	-3.2	90	6.8	
実施例 9	71.5	21.4	0.7	1.14	0.02	1.8	-2.6	93	6.2	
実施例 10	72.0	21.8	0.8	1.15	0.02	1.5	-2.7	92	5.9	
実施例 11										
実施例 1と同じ										
比較例 1	55.6	25.3	0.4	1.08	-0.02	11.4	1.7	87	12.1	
比較例 2	59.4	21.7	0.5	1.07	-0.02	8.1	0.7	88	11.1	
比較例 3	65.1	22.4	0.7	1.09	-0.02	8.0	1.5	88	8.5	
比較例 4	70.9	22.6	0.8	1.09	-0.03	6.0	1.4	88	8.4	
比較例 5	58.0	39.2	1.1	1.13	0.05	13.7	4.8	65	12.1	
比較例 6	59.1	31.4	0.7	1.08	-0.01	11.8	3.3	79	11.4	
比較例 7	44.4	18.6	0.3	1.02	-0.02	14.1	0.8	97	13.1	
比較例 8	77.4	22.5	1.0	1.16	0.02	1.8	-0.7			
比較例 9								93		
									85	

※ 比較例 8 は強度が著しく弱いため、捕集効率、捕集圧損測定のための測定治具に不適合できなかつた。

比較例 1と同じ

[0083]

(Example 11)

In the example 1, the honeycomb structure object (catalyst support) of size:phi229.0 mmxL152.0mm, septum thickness:300micrometer, and cel consistency:46.5 cel / cm² was manufactured like the example 1 except having not performed the process which ***** a through tube.

[0084]

(Example 9 of a comparison)

In the example 1, the honeycomb structure object (catalyst support) of size:phi229.0 mmxL152.0mm, septum thickness:300micrometer, and cel consistency:46.5 cel / cm² was manufactured like the example 1 except having used the cordierite-ized raw material and ostomy agent of the same presentation as the example 1 of a comparison shown in having not performed the process which ***** a through tube, and Table 1 and 2.

[0085]

(Evaluation result)

When a high specific-surface-area alumina and 500g of platinum system oxidation catalysts were supported on each acquired honeycomb structure object and having been considered as the catalyst object, with the honeycomb structure object of an example 11, emission-gas-purification effectiveness was as large as 93%. On the other hand, in spite of having supported a high specific-surface-area alumina and 500g of platinum system oxidation catalysts with the honeycomb structure object of the example 9 of a comparison similarly and having considered as the catalyst object, emission-gas-purification effectiveness was small compared with the honeycomb structure object of 85% and an example 11.

[0086]

[Effect of the Invention] As mentioned above, according to this invention, the porosity honeycomb structure object which can attain effectively improvement in collection efficiency, such as a soot, improvement in the purification engine performance by deployment of a catalyst, reduction of pressure loss, and protraction of uptake time amount, as a result can improve the erosion limitation and AISO static reinforcement at the time of filter playback can be offered. For this reason, it is suitable especially as emission-gas-purification means, such as a diesel particulate filter and catalyst support for emission gas purification.

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the septum in which how to measure fault porosity distribution is shown.

[Drawing 2] It is the graph which shows an example of the fault porosity distribution searched for by the approach shown in drawing 1 .

[Drawing 3] It is the graph which shows the result of having carried out the Fourier transform of the fault porosity distribution shown in drawing 2 by each series.

[Drawing 4] It is the graph which shows the relation between porosity and a length-of-developed-blank ratio by each example and the example of a comparison.

[Drawing 5] It is the graph which shows the relation between porosity and the average (X) of a primary component magnitude spectrum (S) and a secondary component magnitude spectrum (F) by each example and the example of a comparison.

[Drawing 6] It is the graph which shows the average (X) of a primary component magnitude spectrum (S) and a secondary component magnitude spectrum (F), and relation with a soot uptake pressure loss by each example and the example of a comparison.

[Translation done.]

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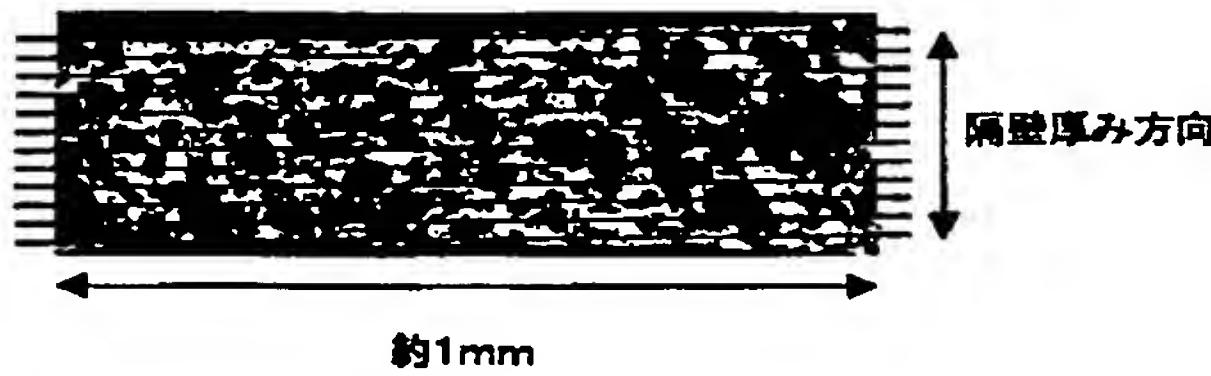
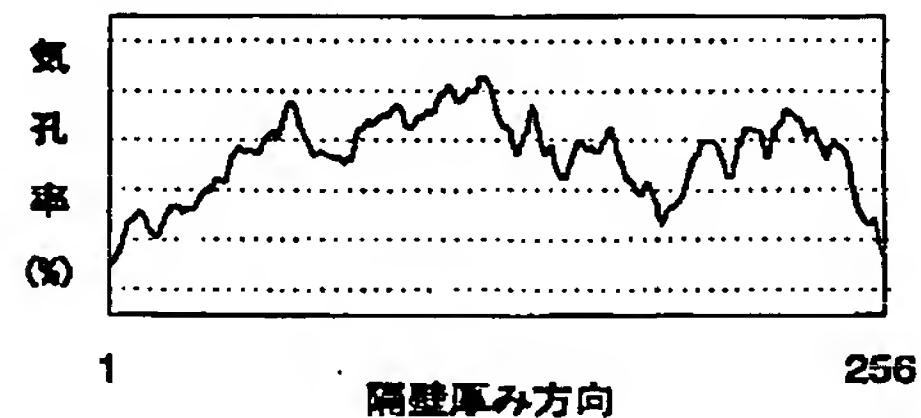
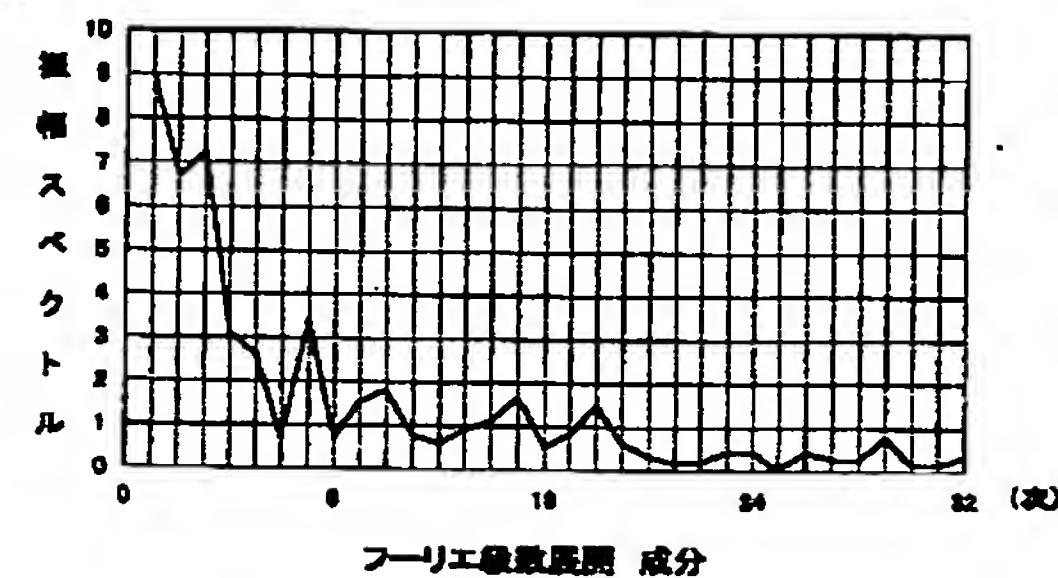
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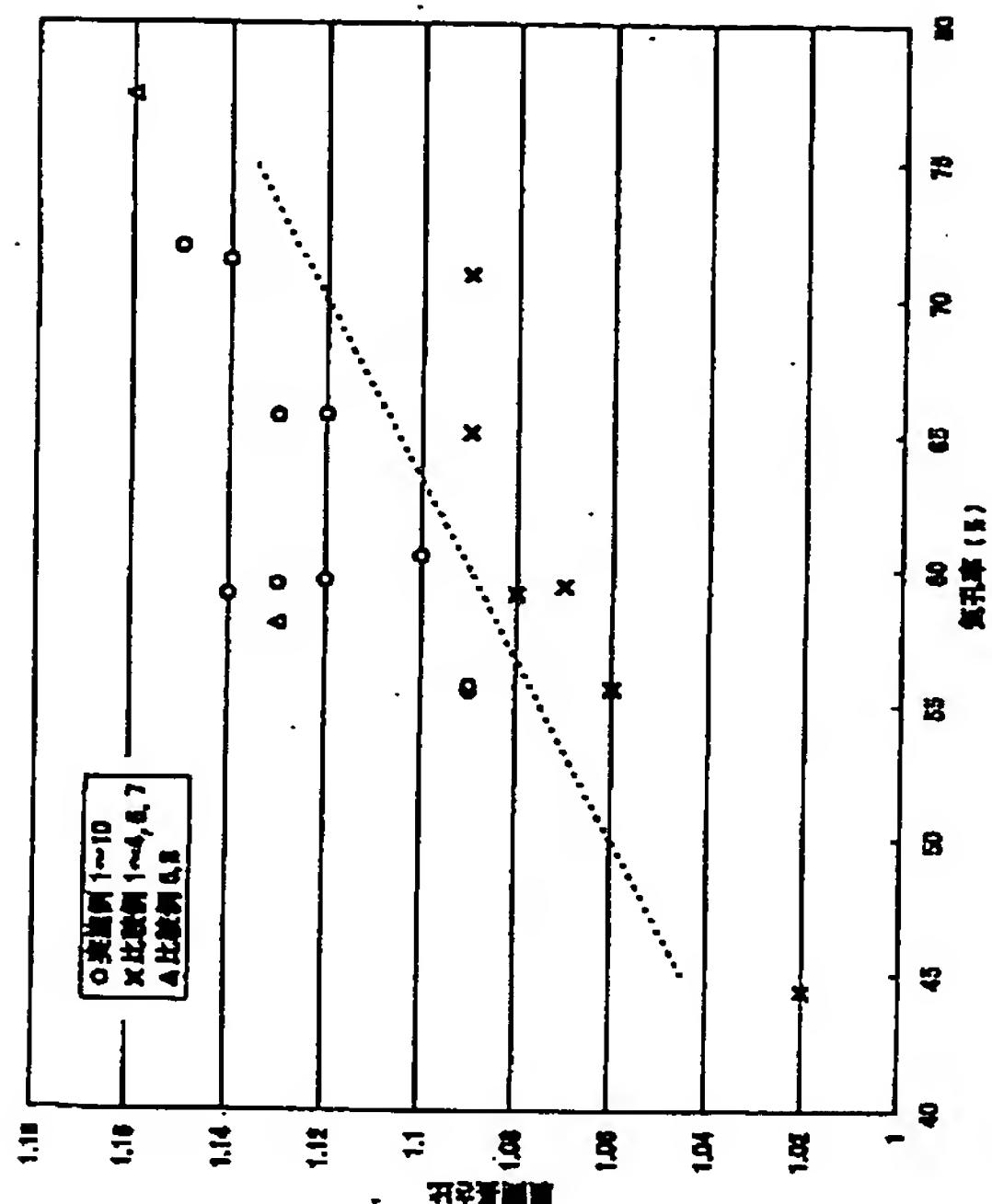
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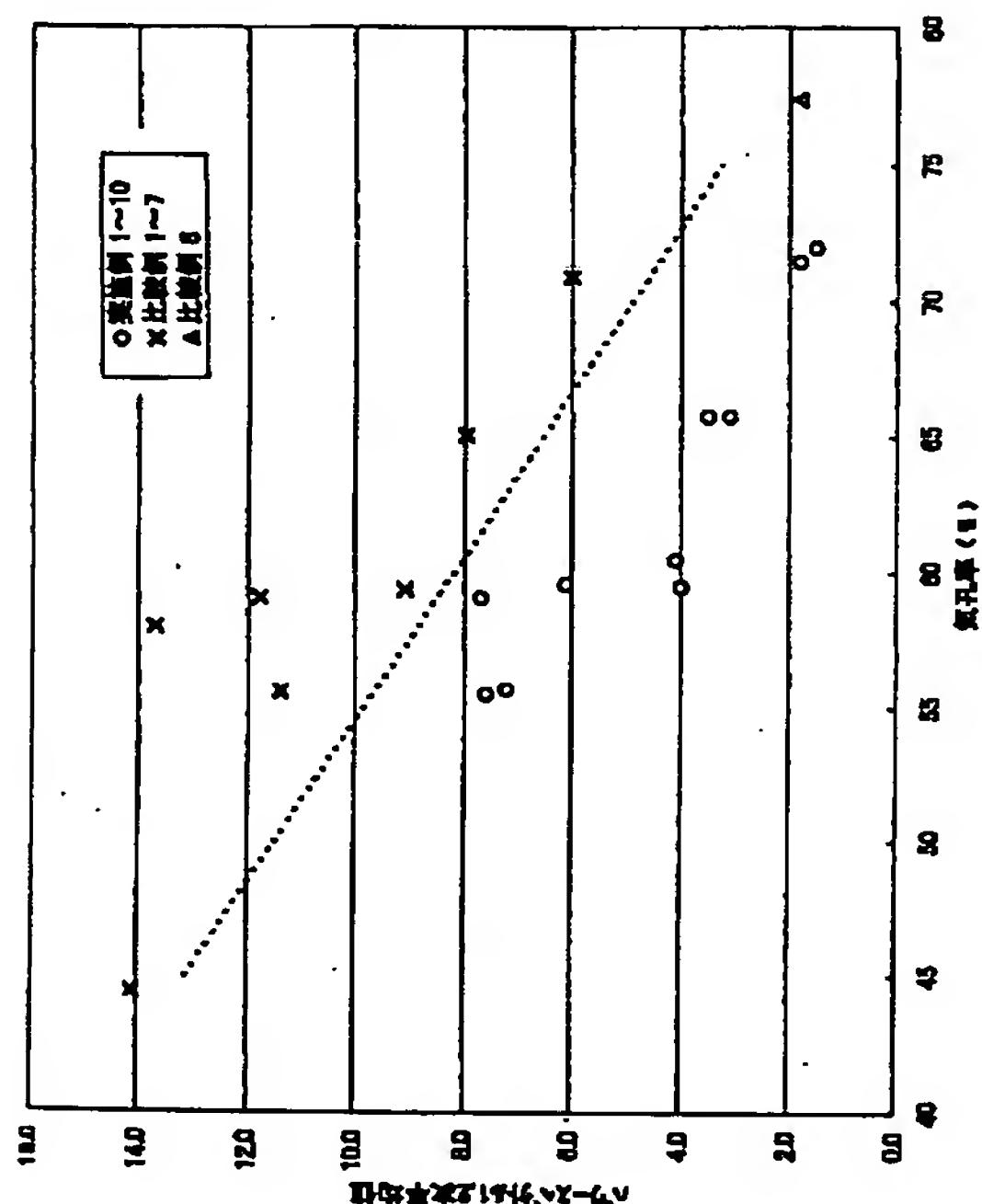
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DRAWINGS

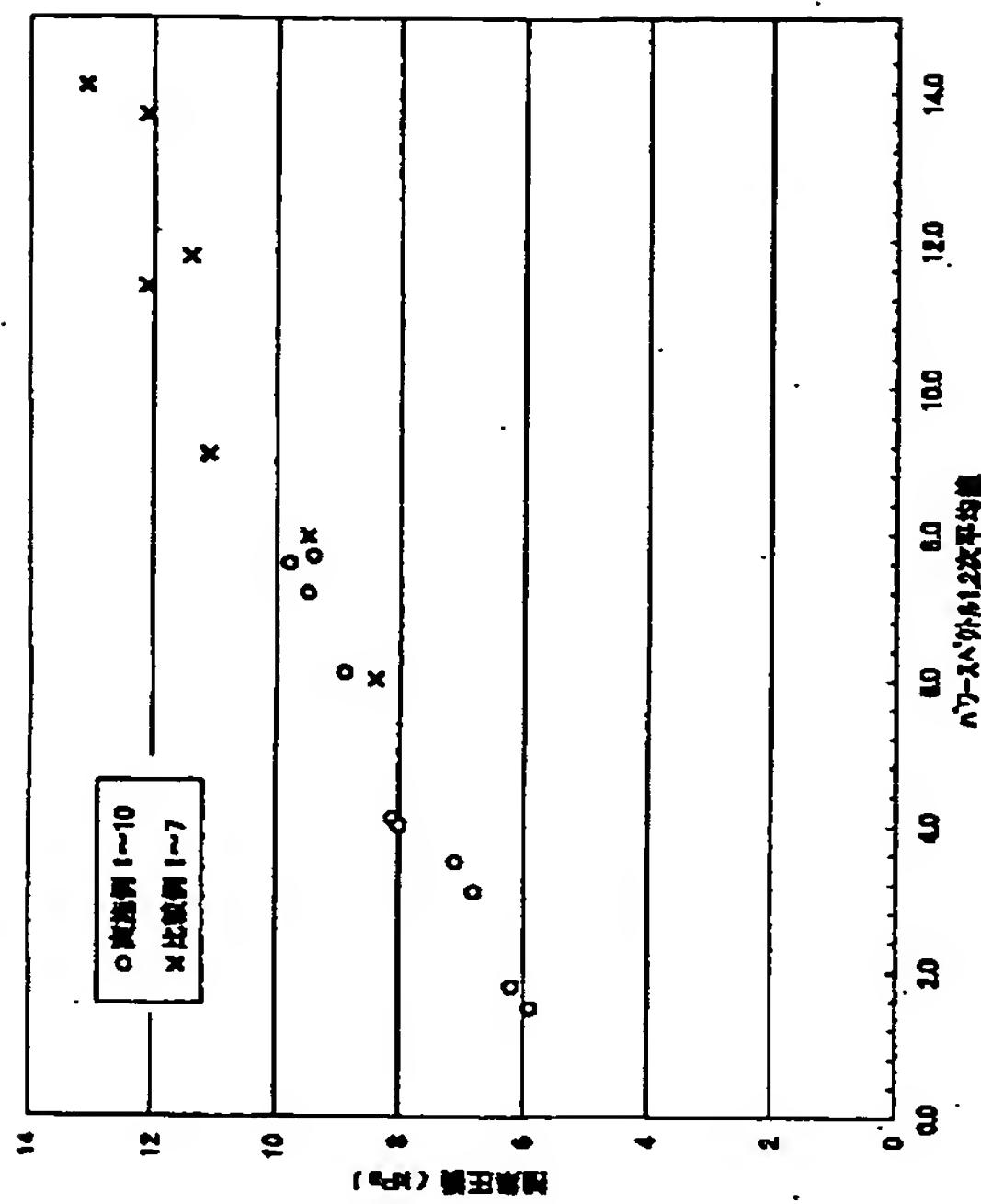
[Drawing 1]**[Drawing 2]****[Drawing 3]****[Drawing 4]**



[Drawing 5]



[Drawing 6]



[Translation done.]

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(54) 【発明の名称】多孔質ハニカム構造体

(57) 【要約】

【課題】スト等の捕集効率の向上、圧力損失の低減、触媒の有効利用による浄化性能の向上、及び捕集時間の長期化を効果的に達成することができ、延いてはフィルター再生時における溶損限界及びアイソスタティック強度を向上させることができる多孔質ハニカム構造体を提供する。

【解決手段】コーディエライトを主成分とし、気孔率55～75%、平均気孔径1.5～3.5 μmで、下記条件式(1)に示す気孔分布を有する多孔質セラミックスの隔壁を備える多孔質ハニカム構造体とする。

【数1】

$$L_r > 0.3 \times P / 100 + 0.91 \quad (1)$$

10

「上記条件式(1)中、 L_r は、平均展開長さ比を意味する。また、 P は、水銀圧入式ボロシメーターで全気孔容積を測定し、コーディエライトの真比重を2.52 g/ccとした際に、当該全気孔容積から求められる気孔率を意味する。」

【選択図】 なし

【特許請求の範囲】

【請求項 1】

コーディエライトを主成分とし、気孔率 55 ~ 75 %、平均気孔径 15 ~ 35 μm の多孔質セラミックスからなる複数の隔壁を備える多孔質ハニカム構造体であって、該隔壁の気孔が、下記条件式(1)に示す気孔分布を有することを特徴とする多孔質ハニカム構造体。

【数1】

$$L_r > 0.3 \times P / 100 + 0.91 \quad (1)$$

「上記条件式(1)中、 L_r は、下記数式(2)により求められる平均展開長さ比を意味する。また、 P は、水銀圧入式ポロシメーターで全気孔容積を測定し、コーディエライトの真比重を 2.52 g / cc とした際に、当該全気孔容積から求められる気孔率を意味する。」¹⁰

【数2】

$$L_r = L_o / 4 \quad (2)$$

「上記数式(2)中、 L_o は、表面粗さ測定機を用い、隔壁表面の任意の 10箇所について隔壁表面に沿って 4 mm (隔壁表面に開口した気孔の存在を無視した直線長さ) 触針して求めた平均展開長さ (隔壁表面に開口した気孔の表面を含めた長さの平均値) を意味し、 L_r は、平均展開長さ比を意味する。」²⁰

【請求項 2】

前記隔壁の気孔が、隔壁厚さ方向に、下記条件式(3)に示す断層気孔分布を有する請求項1に記載の多孔質ハニカム構造体。

【数3】

$$X < -3.3 \times P / 100 + 2.8 \quad (3)$$

「上記条件式(3)中、 X は、下記数式(4)及び(5)から求められる一次成分振幅スペクトル (F) と、二次成分振幅スペクトル (S) との平均値である。また、 P は、水銀圧入式ポロシメーターで全気孔容積を測定し、コーディエライトの真比重を 2.52 g / cc とした際に、当該全気孔容積から求められる気孔率を意味する。」³⁰

【数4】

$$F = \sqrt{X_{SRe}(1)^2 + X_{SIm}(1)^2} \quad (4)$$

「上記数式(4)中、 F は、下記変換式(6)において、 $k = 1$ とした際の一次成分振幅スペクトルを表わす。また、 $X_{SRe}(1)$ 、及び $X_{SIm}(1)$ は、下記変換式(6)において、 $k = 1$ とした際の実数部と虚数部をそれぞれ示す。」

【数5】

$$S = \sqrt{X_{SRe}(2)^2 + X_{SIm}(2)^2} \quad (5)$$

「上記数式(5)中、 S は、下記変換式(6)において、 $k = 2$ とした際の二次成分振幅スペクトルを表わす。また、 $X_{SRe}(2)$ 、及び $X_{SIm}(2)$ は、下記変換式(6)において、 $k = 2$ とした際の実数部と虚数部をそれぞれ示す。」⁴⁰

【数6】

$$X_s(k) = \sum_{n=0}^{255} x(n) \left(\cos \frac{2\pi k}{256} \cdot n - j \sin \frac{2\pi k}{256} \cdot n \right) \quad (6)$$

「上記変換式(6)中、 $X_s(k)$ は離散フーリエ変換を表わし、 k は次数を表わす。また、 n は、0～255の整数であり、隔壁断面を隔壁最表面部($n=0$)から厚さ方向へ順に256分割した際の分割位置を表わす。また、 $X(n)$ は、分割位置 $n \sim n+1$ までの隔壁断面領域で気孔部分が占める面積比率を表わす。」

【請求項3】

前記隔壁が、 $350 \mu\text{m}$ 以下の厚さである請求項1又は2に記載の多孔質ハニカム構造体。

【請求項4】

40～800°Cにおける熱膨張係数が、 $1.0 \times 10^{-6} / \text{°C}$ 以下である請求項1～3のいずれか一項に記載の多孔質ハニカム構造体。

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【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、多孔質ハニカム構造体及びその製造方法に関する。より詳しくは、隔壁の気孔分布を制御することにより、捕集時間の長期化、捕集効率の向上、及び圧力損失の低減を効果的に達成でき、延いてはフィルター再生時における溶損の防止やアイソスタティック強度の向上が可能な、排ガス浄化用のフィルター、並びに浄化性能の向上や圧力損失の低減を効果的に達成することができるとともに、アイソスタティック強度に優れる触媒担体、として適用できる多孔質ハニカム構造体に関する。

【0002】

【従来の技術】自動車用エンジン、特に、ディーゼルエンジン等から排出される粒子状物質やNO_xの環境への影響が最近大きくクローズアップされてきており、このような有害物質を除去する重要な手段として、多孔質ハニカム構造体の利用が種々検討されている。

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【0003】例えば、多孔質の隔壁により仕切られた複数の貫通孔を有するハニカム構造体において、貫通孔が開孔する両端面で互いに異なる位置で目封じした構造とし、一の端面に開口する各貫通孔に排ガスを流入させて、強制的にハニカム構造体内の隔壁を通過させることにより、排ガス中の粒子状物質を捕集、除去するハニカムフィルターが開発されている。また、触媒担持量を増大させることにより、浄化性能を向上させる新たな試みとして、全隔壁を高気孔率の多孔質体として、HCやNO_xを分解する触媒を担持させたハニカム構造の触媒体も開発が進められている。

【0004】ところで、当該多孔質ハニカム構造体にあっては、フィルターとしての用途では、当然に、高い捕集効率を求められる。また、隔壁表面に開口する気孔に一定以上のストートが堆積すると、急激に圧力損失が増大するため、通常、一定時間使用後に高温で燃焼してストートを焼失させる再生工程が行われるが、この再生工程が高頻度で行われると多孔質ハニカム構造体の劣化が促進されるため、捕集時間を長くして再生工程の回数を低減することが求められている。

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【0005】更に、フィルターとしての用途では、フィルター再生時に多孔質ハニカム構造体が極めて高温化に曝されるため、当該フィルター再生による隔壁の溶損を防止するには、フィルター全体について一定以上の熱容量を有することが好ましく、ストートを燃焼させ、当該フィルターを再生する際に隔壁の溶損を引き起こさない最大のストート量(ストート限界再生量)が大きいことが望まれる。

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【0006】他方、触媒担体としての用途では、近年、排ガス浄化性能をより向上させるために触媒担持量を増大させることが要請されており、高気孔率化したハニカム構造体に触媒を担持する試みが行われている。

【0007】また、何れの用途においても、低燃費化及び高出力化の要請が強いディーゼルエンジン等の燃焼機関に設置される多孔質ハニカム構造体にあっては、圧力損失の低減化が求められている。更にまた、何れの用途においても、多孔質ハニカム構造体は、大きな振動を継続的に受けるエンジンの近傍に設置されることから、金属ケース内に強固に把持する必要があり、ハニカム構造体全体について高いアイソスタティック強度が要求される。

【0008】従来、このような要請に応じるべく、隔壁の気孔分布を様々な範囲で制御し

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たハニカム構造体等が開示されている。

【0009】 例え、特許文献1には、隔壁表面に開口する気孔の比表面積 (Mm^2/g) と、そのフィルター表面における表面粗さ ($N\mu m$) とを、 $1000M + 85N \geq 530$ に制御したハニカム構造体が開示されている。

【0010】 しかし、このハニカム構造体は、シリカ、タルク等のセラミックス原料の粒径を制御したセラミックス原料を用いて製造されるものであり、気孔率が最大でも60%程度であった(特許文献1)。

【0011】 また、このハニカム構造体は、隔壁全体の気孔率と隔壁表面に開口する気孔の比率以外の隔壁内部における気孔の分布については、何ら考慮するものではなく、捕集時間の長期化、捕集効率の向上、浄化性能の向上、及び圧力損失の低減といった要請を充分に満足し得るものではなかった。
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【0012】 これに対して、コーディエライト化原料に、造孔剤として、有機発泡剤と、カーボンとを添加した原料を用いて、隔壁表面の気孔を、 $40 \sim 100\mu m$ の大孔に対して、 $5 \sim 40\mu m$ の小孔の数を5~40倍としたコーディエライトハニカム構造体(特許文献2)が提案されている。

【0013】 しかし、このハニカム構造体も、隔壁全体の気孔率に対する隔壁表面に開口する気孔の比率については何ら考慮するものではなかった。また、このハニカム構造体では、造孔材として、最初は密な粒子で、加熱により中空化する有機発泡剤を用いて製造されていた。このため、押出し成形直後に隔壁表面に開口する有機発泡剤は少なく、その後の乾燥工程等でバインダーが熱でゲル化し成形体が硬化すると、 $100^{\circ}C$ 以下の比較的低温で発泡するものでも、隔壁表面を突き破るほど大きく膨張するまでには至らず、隔壁表面に開口する気孔が少ないので現状であった。この結果、このハニカム構造体では、隔壁の厚さ方向における気孔分布に偏りを有し、捕集効率の向上、捕集時間の長期化、及び圧力損失の低減といった要請を充分に満足し得るものではなかった。また、この気孔分布の偏りによって、隔壁内部で担持される触媒の量が非常にいため、浄化反応に実際に寄与する有効利用率が小さく充分な浄化性能が得られなかった。更に、このような問題を解決すべく、隔壁全体の更なる高気孔率化を図ると、アイソスタティック強度の低下や熱容量低下によるフィルター再生時における局所的な隔壁の溶損を生じるという問題があった。
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【0014】 また、PMMA、PET等の非発泡系の造孔剤を用いて製造したハニカム構造体でも、上記同様、隔壁表面に開口する気孔は少ないので現状であり、効果的に、捕集効率の向上、捕集時間の長期化、浄化性能の向上、及び圧力損失の低減といった要請を充分に満足し得るものではなく、隔壁全体の更なる高気孔率化を図った場合には、アイソスタティック強度の低下や熱容量低下によるフィルター再生時における局所的な隔壁の溶損を生じるという問題があった。
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【0015】

【特許文献1】

特許第2726616号公報

【特許文献2】

特開平9-77573号公報

【0016】

【発明が解決しようとする課題】 本発明は、上述の問題に鑑みなされたものであり、スト等の捕集効率の向上、触媒の有効利用による浄化性能の向上、圧力損失の低減、及び捕集時間の長期化を効果的に達成することができ、延いてはフィルター再生時における溶損限界及びアイソスタティック強度を向上することができる多孔質ハニカム構造体を提供することを目的とする。

【0017】

【課題を解決するための手段】 本発明者は、上述の課題を解決するべく鋭意研究した結果、発泡済みの発泡樹脂を添加した坯土を用いてハニカム構造体を製造したところ、高気孔率で、しかも隔壁表面に開口する気孔が多数形成され、隔壁展開長さ比が全体の気孔率に対して特定値以上となる気孔分布のハニカム構造体が得られ、当該ハニカム構造体によれ
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ば、上述した従来の課題を解決し得るという知見に至り、本発明を完成した。

【0018】即ち、本発明によれば、コーディエライトを主成分とし、気孔率55～75%、平均気孔径15～35μmの多孔質セラミックスからなる複数の隔壁を備えるハニカム構造体であって、当該隔壁の気孔が、下記条件式(1)（以下、単に「条件式(1)」ということがある。）に示す気孔分布を有することを特徴とする多孔質ハニカム構造体が提供される。

【0019】

【数7】

$$L_r > 0.3 \times P / 100 + 0.91 \quad (1)$$

【0020】「上記条件式(1)中、 L_r は、下記数式(2)（以下、単に「数式(2)」ということがある。）により求められる平均展開長さ比を意味する。また、 P は、水銀圧入式ポロシメーターで全気孔容積を測定し、コーディエライトの真比重を2.52g/ccとした際に、当該全気孔容積から求められる気孔率を意味する。」

【0021】

【数8】

$$L_r = L_0 / 4 \quad (2)$$

【0022】「上記数式(2)中、 L_0 は、表面粗さ測定機を用い、隔壁表面の任意の10箇所について隔壁表面に沿って4mm（隔壁表面に開口した気孔の存在を無視した直線長さ）触針して求めた平均展開長さ（隔壁表面に開口した気孔の表面を含めた長さの平均値）を意味し、 L_r は、平均展開長さ比を意味する。」

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【0023】また、本発明においては、更に、当該隔壁の気孔が、隔壁厚さ方向に、下記条件式(3)（以下、単に「条件式(3)」ということがある。）に示す断層気孔分布を有するものが好ましい。

【0024】

【数9】

$$X < -3.3 \times P / 100 + 28 \quad (3)$$

【0025】「上記条件式(3)中、 X は、下記数式(4)及び(5)（以下、それぞれ「数式(4)」、「数式(5)」ということがある。）から求められる一次成分振幅スペクトル(F)と、二次成分振幅スペクトル(S)の平均値である。また、 P は、前記条件式(1)の場合と同様にして求められる気孔率を意味する。」

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【0026】

【数10】

$$F = \sqrt{X_{sR\text{e}}(1)^2 + X_{sI\text{m}}(1)^2} \quad (4)$$

【0027】「上記数式(4)中、 F は、下記変換式(6)において、 $k = 1$ とした際の一次成分振幅スペクトルを表わす。また、 $X_{sR\text{e}}(1)$ 、及び $X_{sI\text{m}}(1)$ は、下記変換式(6)において、 $k = 1$ とした際の実数部と虚数部をそれぞれ示す。」

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【0028】

【数11】

$$S = \sqrt{X_{sR\text{e}}(2)^2 + X_{sI\text{m}}(2)^2} \quad (5)$$

【0029】「上記数式(5)中、 S は、下記変換式(6)において、 $k = 2$ とした際の二次成分振幅スペクトルを表わす。また、 $X_{sR\text{e}}(2)$ 、及び $X_{sI\text{m}}(2)$ は、下記変換式(6)において、 $k = 2$ とした際の実数部と虚数部をそれぞれ示す。」

【0030】

【数12】

$$X_s(k) = \sum_{n=0}^{255} x(n) \left(\cos \frac{2\pi k}{256} \cdot n - j \sin \frac{2\pi k}{256} \cdot n \right) \quad (6)$$

【0031】「上記変換式(6)中、 $X_s(k)$ は離散フーリエ変換を表わし、 k は次数を表わす。また、 n は、0～255の整数であり、隔壁断面を隔壁最表面部($n=0$)から厚さ方向へ順に256分割した際の分割位置を表わす。また、 $X(n)$ は、分割位置 n ～ $n+1$ までの隔壁断面領域で気孔部分が占める面積比率を表わす。」

【0032】本発明においては、隔壁の厚さを350μm以下とすることが好ましい。また、ハニカム構造体全体について、40～800℃における熱膨張係数を、 $1.0 \times 10^{-6}/\text{°C}$ 以下とすることができる。

【0033】

【発明の実施の形態】以下、本発明の実施の形態を、具体的に説明する。

【0034】本発明の多孔質ハニカム構造体は、コーディエライトを主成分とし、特定の気孔率及び平均気孔径の気孔を有し、更に各隔壁表面の展開長さ比と気孔率とが特定の条件式を満たす気孔率分布を有するものである。以下、具体的に説明する。

【0035】本発明において、隔壁の主成分たるコーディエライトは、配向、無配向、 α 結晶質、 β 結晶質等のいずれでもよい。また、コーディエライト以外の成分として、例えば、ムライト、ジルコン、チタン酸アルミニウム、クレーボンド炭化ケイ素、ジルコニア、スピネル、インディアライト、サフィリン、コランダム、又はチタニア等を1種単独又は2種以上含有するものであってもよい。

【0036】また、本発明においては、ハニカム構造体の隔壁が、気孔率55～75%、より好ましくは気孔率65～75%の高気孔率セラミックスで構成される。

【0037】気孔率が55%未満であると、隔壁における排ガスに対する透過抵抗が大きすぎるため、後述するように気孔分布を制御しても実用上支障のない程度まで圧力損失を低減することが困難となる。また、所望の触媒端持量を得ることも困難となる。一方、気孔率が75%を超えると、アイソスタティック強度が低くなり、ケースへの把持の際に破損を生じ易くなる。

【0038】また、本発明においては、この多孔質セラミックスの隔壁に存在する気孔が、平均気孔径15～35μmのものである。

【0039】平均気孔径が15μm未満であると、捕集効率は高くなるものの、初期圧損が大きくなる。一方、平均気孔径が35μmを超えると、後述の如く気孔分布を制御しても、実用上要求される捕集効率を確保することが困難となる。また、隔壁内部にストートが堆積し易く、再生処理の際に隔壁内部にストートが燃え残り易いため、再生処理後であっても、ストート堆積圧損が低くならない場合がある。

【0040】本発明のハニカム構造体は、更に、各隔壁表面の展開長さ比が隔壁全体の気孔率に対して特定の数値以上となる気孔分布、具体的には、前記条件式(1)の条件を満たす気孔分布を有している。

【0041】これにより、全気孔中、実質的に有用なストート堆積許容容積が大きくなるため、効果的に捕集効率を向上し、かつ捕集時間を長くすることができる。また、隔壁全体の気孔率に対する隔壁表面に開口する気孔の割合が多いため、効果的に圧力損失を低減し、又は触媒担持量の増大や担持した触媒の有効利用率の増大によって効果的に浄化性能を向上することができる。また、以上のことから明らかのように、ある程度隔壁全体の気孔率を低くしても、捕集効率、捕集時間、浄化性能、及び圧力損失について充分な特性を得ることが可能であり、延いてはアイソスタティック強度やストート限界再生量を増大させることができる。

【0042】本発明の多孔質ハニカム構造体における隔壁は、更に、厚さ方向の断層気孔分布が、前記条件式(3)に示す気孔分布を有しているものが、フィルター再生時の隔壁溶損、アイソスタティック強度、捕集効率、浄化性能、圧力損失、及び捕集時間といったハニカム構造体に求められる諸特性を総合的に更に向上させることができる点で好ましい

【0043】即ち、前記条件式(3)の条件を満たすハニカム構造体は、断層気孔率分布の変動が小さく隔壁の存在する気孔が、隔壁内部に偏在せずに均一に分布しており、従って、隔壁内部に殆どストートが堆積せず、フィルター再生後に残存するストート量も少ないため、ストート堆積圧損を更に小さくすることができる。また、前記条件式(3)の条件を満たすハニカム構造体は、隔壁各部で局所的にアイソスタティック強度の低下や熱容量の減少によるストート限界再生量の低下を招くことはないため、これらの特性を満足させながら、捕集効率の向上、捕集時間の長期化、及び圧力損失の低減をより高レベルで達成することができる。同様に、触媒担持量や担持した触媒の有効利用率を更に増大させてるので、アイソスタティック強度を満足させながら、より高い浄化性能を達成することができる。
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【0044】ここで、前記変換式(6)中に示す隔壁厚さ方向における断層気孔率分布は、走査型電子顕微鏡(SEM)により測定することができる。具体的には、まず、ハニカム構造体の隔壁断面を倍率100倍で観察し、その画像データを画像解析ソフトで2値化処理し、黒色部を気孔部分、白色部をハニカム基材部分とする。そして、図1に示すように、隔壁長さ方向に1mmの幅で、断面を隔壁厚さ方向に256分割し、分割された各断層面領域毎に気孔部分が占める面積の比率を算出して求める。図2に、このようにして求めた断層気孔率分布X(n)の一例を、図3に、図2に示す断層気孔率分布X(n)を各級数でフーリエ変換した結果を示す。

【0045】本発明においては、ハニカム構造体の隔壁厚さ、セル形状、セルピッチ等、隔壁が有する気孔の各種条件以外の点については特に制限はなく、用途等に応じて好適な設計とすればよい。もっとも、所望のフィルター機能を付与するためには、排ガス流入側端面と排ガス排出側端面に開口する複数の貫通孔を、両端面で相互に異なる位置で目封じした構造とすることが好ましい。
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【0046】また、ハニカム構造体の多孔質の隔壁に、触媒を担持して触媒体とすることができる。触媒担体として用いる場合には、セル密度は6~1500セル/インチ²(0.9~233セル/cm²)、隔壁の厚さは50~2000μm(約2~79mm)の範囲とすることが好ましい。また触媒担体として用いる場合の軸方向(排ガス流れ方向)長さは、通常は、60~300mm、好ましくは、100~250mmである。

【0047】また、触媒担体には、吸着層を設けてもよく、通常は、高比表面積を有するアルミナ、ゼオライトを主成分とするものが好適に使用される。ゼオライトは天然品、合成品のいずれでも良く、また種類は特に限定されないが、耐熱性、耐久性、疎水性の点で、Si/Ai比が40以上のものが好適に用いられる。具体的にはZSM-5、USY、 β -ゼオライト、シリカライト、メタロシリケート等が好適に使用できる。
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【0048】また、触媒成分はハニカム構造体に直接担持させてもよく、また、吸着層に担持させてもよい。

【0049】本発明においては、隔壁全体について均一な気孔分布を有し、前述したように、ある程度低気孔率化も可能であることから、隔壁をより薄くしても隔壁の溶損を防止し、所望のアイソスタティック強度を確保することができる。従って、隔壁厚さを350μm以下とすることで圧力損失がより小さい、又は触媒有効利用率の高い多孔質ハニカム構造体とができる。
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【0050】また、本発明のハニカム構造体は、隔壁表面付近の気孔を形成する手段として、コーディエライト化反応を阻害しない発泡済みの発泡樹脂を用いることで、40~800℃における熱膨張係数が $1.0 \times 10^{-6}/\text{℃}$ 以下とすることができ、高温使用における耐熱衝撃性を向上させることができる。

【0051】本発明において、上述した気孔分布とする方法としては、コーディエライト化原料に、造孔剤として、アクリル系マイクロカプセル等の発泡済みの発泡樹脂を添加、混練した坯土を用いて製造する方法が好ましい。

【0052】当初から中空の発泡済みの発泡樹脂を添加した坯土を用いると、当該坯土の押出し成形直後、押圧力から解放された発泡済みの発泡樹脂が、隔壁内で膨張するため、隔壁表面近くに存在するものは、隔壁表面からはみ出して膨張し、最終的にはその外壁が
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破裂して隔壁表面に開口する気孔が多数形成されることとなる。また、乾燥前の状態で、既に多数の気孔が形成されていると同様の状態であるため、その後の乾燥工程等でバインダーのゲル化によりハニカム成形体が硬化しても、それによって隔壁表面に開口する気孔の数が低減することはない。

【0053】もっとも、本発明においては、タルク、シリカ等のセラミックス原料について粒径を制御して、得られるフィルターの気孔率及び平均気孔径を制御する方法を組合わせることもできる。但し、用いる粒径が大きすぎる場合には、発泡済みの発泡樹脂を併用しても、所望の気孔分布とすることが困難となるので、タルクであれば、粒径 $50\text{ }\mu\text{m}$ 以下のもの、シリカであれば、粒径 $100\text{ }\mu\text{m}$ 以下のものを用いることが好ましい。

【0054】また、本発明においては、造孔剤として、例えば、カーボン、小麦粉、澱粉、フェノール樹脂、ポリメタクリル酸メチル、ポリエチレン、又はポリエチレンテレフタレート等の他の材料を含有させてもよい。中でも、グラファイト等のカーボンは、バインダーや発泡樹脂が酸化分解して発熱を引き起こす温度域と異なる温度域で燃焼するため、焼成切れを発生させにくい点で好ましい。10

【0055】また、発泡済みの発泡樹脂を造孔剤として単独で用いられる場合には、コーディエライト化原料 100 質量部に対して発泡済みの発泡樹脂を $0.5 \sim 5$ 質量部含有させることが好ましく、 $1 \sim 3.5$ 質量部含有させることがより好ましい。

【0056】発泡済みの発泡樹脂の含有量が 0.5 質量部未満であると、気孔率が 55% 未満となり得られるハニカム構造体の圧力損失が大きくなる。一方、発泡済みの発泡樹脂の含有量が 5 質量部を超えると、気孔率が 75% より大きくなり、得られるハニカム構造体のアイソスタティック強度及び熱容量が低下して実用に耐え難くなる。20

【0057】更に、グラファイト等のカーボンと発泡済みの発泡樹脂を併用する場合には、同様の点から、コーディエライト化原料 100 重量部に対して、カーボンを $5 \sim 25$ 重量部、発泡済みの発泡樹脂を $0.5 \sim 3$ 重量部含有させることが好ましく、カーボンを $5 \sim 15$ 重量部、発泡済みの発泡樹脂を $1 \sim 3$ 重量部含有させることがより好ましい。

【0058】本発明においては、通常、この他の添加剤として、ヒドロキシプロピルメチルセルロース、メチルセルロース、ヒドロキシエチルセルロース、カルボキシルメチルセルロース、若しくはポリビニルアルコール等のバインダー、又はエチレングリコール、デキストリン、脂肪酸石鹼、ポリアルコール等の分散剤等を含有させることが好ましい。なお、本発明においては、乾燥工程におけるバインダーのゲル化によって成形体が硬化しても、気孔分布の偏りが生じないことは前述した通りである。30

【0059】

【実施例】以下、本発明を実施例により具体的に説明するが、本発明はこれら実施例に何ら限定されるものではない。なお、各実施例及び各比較例で得られたハニカム構造体について以下に示す方法で評価を行った。

【0060】

1. 評価方法

(1) 気孔の平均孔径

マイクロメリティックス社製の水銀圧入式ポロシメーターで測定した。

【0061】

(2) 気孔率

マイクロメリティックス社製の水銀圧入式ポロシメーターで全気孔容積を測定し、コーディエライトの真比重を 2.52 g/cc として、当該全気孔容積から、気孔率を計算した。

【0062】

(3) 平均展開長さ比

テーラーホプソン社製のFTS-S4C型表面粗さ測定機を用いて、任意に選択した 10 箇所の隔壁表面で、 $2\text{ }\mu\text{mR}$ の触針先端を隔壁表面に沿って、隔壁表面の直線長さ（開口した気孔の存在を無視した長さ）で 4 mm 接触させ、当該直線長さに対応する展開長さ（開口した気孔の内面を考慮した長さ）を測定した。次いで、 10 箇所の隔壁表面における

展開長さの平均値 (L_0) を求め、この平均展開長さ (L_0) を直線長さの 4 で除して平均展開長さ比 (L_r) を求めた。また、単位気孔率当たりの平均展開長さ比は、この平均展開長さ比を、前述した方法で求めた隔壁全体の気孔率で除して求めた。

【0063】

(4) 断層気孔率の均一性 (一次成分振幅スペクトル (S) と二次成分振幅スペクトル (F) の平均値 (X))

図1に示すように、ハニカム構造体の隔壁断面を、隔壁長さ方向に 1 mm の範囲で SEM で撮影し、その画像データを画像解析ソフトで 2 値化処理し、黒色部を気孔部分、白色部をハニカム基材部分とした。その後、 $300 \mu\text{m}$ の隔壁を厚さ方向に 256 分割し、分割された各領域 ($n \sim n + 1$) における気孔部分の面積比率を図2に示すように隔壁表面から順に算出した。次いで、隔壁厚さ方向における気孔部分の面積比率の変化をフーリエ解析して、周波数 (n) = 1, 2 の波として各波の振幅スペクトルを求め、それぞれ一次成分振幅スペクトル (S)、及び二次成分振幅スペクトル (F) とした。最後に、これらの数値の平均値 (X) を求め、断層気孔率の均一性を評価した。

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【0064】

(5) 捕集効率

ストージェネレーターによりストートを発生させた排ガスを、各実施例及び比較例で得られたハニカム構造体に、一定時間 (2分) 通過させ、フィルター通過後排ガスに含まれるストートを濾紙で捕集し、ストートの重量 (W^1) を測定した。また、同じ時間、ストートを発生させた排ガスを、フィルターを通過させずに濾紙で捕集し、ストートの重量 (W^2) を測定した。次いで、得られた各重量 (W^1) (W^2) を以下に示す式 (7) に代入して捕集効率を求めた。

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【0065】

【数13】

$$(W^2 - W^1) / (W^2) \times 100 \quad (7)$$

【0066】

(6) スート捕集圧損

まず、各実施例及び比較例で得られたハニカム構造体の両端面に、内径 $\phi 130 \text{ mm}$ のリングを圧接し、このリングを介して、ストージェネレーターで発生させたストートを、ハニカム構造体の $\phi 130 \text{ mm}$ の範囲内に流入し、10 g のストートを捕集させた。次いで、ハニカム構造体がストートを捕集した状態で、 $2.27 \text{ Nm}^3 / \text{min}$ の空気を流し、フィルター前後の圧力差を測定して、ストートを捕集した状態での圧力損失を評価した。

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【0067】

(7) 排ガス浄化効率

各実施例及び比較例で得られたハニカム構造体に触媒を担持した触媒体をメタルケースにキャニングし、5リットルディーゼルエンジンを用いて、HCの浄化効率を評価した。エンジンからの排ガスをハニカム構造の触媒体に流し、触媒体に導入前の排ガス中のHC濃度B1、及び触媒体通過後の排ガス中のHC濃度B2を測定し、 $100 \times (B_1 - B_2) / B_1$ の計算式により、排ガス浄化効率を求めた。

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【0068】

2. 実施例、及び比較例、並びに評価結果

(実施例1)

表1に示す平均粒径及び粒径分布のタルクB (平均粒径: $45 \mu\text{m}$)、カオリン ($10 \mu\text{m}$)、アルミナ (平均粒径: $5 \mu\text{m}$)、水酸化アルミニウム (平均粒径: $3 \mu\text{m}$)、及び溶融シリカB (平均粒径: $40 \mu\text{m}$) を、表2に示すように、タルクB 40 質量%、カオリン 20 質量%、アルミナ 14 質量%、水酸化アルミニウム 16 質量%、溶融シリカB 10 質量%の割合で混合してコーディエライト化原料を調製した。

【0069】次いで、表2に示すように、このコーディエライト化原料 100 質量部に対して、アクリロニトリル-メチルメタクリレート共重合体からなる発泡済みの発泡樹脂を 2 質量部、ヒドロキシプロピルメチルセルロース 4 質量部、ラウリン酸カリ石鹼 0.5 質量部、

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量部、水30質量部を投入、混練して可塑性とし、この可塑性の原料を、真空土練機でシリンダー状の坯土を成形し、押出し成形機に投入してハニカム状に成形した。

【0070】次いで、得られた成形体を、誘電乾燥の後、熱風乾燥で絶乾し、所定の寸法に両端面を切断した。

【0071】次いで、このハニカム状の乾燥体における貫通孔を、同様の組成のコーディエライト化原料からなるスラリーで、貫通孔が開口する両端面で互い違いに目封じした。

【0072】最後に、1420℃、4時間、焼成して、サイズ：Φ144mm×L152mm、隔壁厚さ：300μm、セル数：300セル/inch²のハニカム構造体（ハニカムフィルター）を得た。

【0073】

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（実施例2～10、及び比較例1～8）

実施例1において、表1及び表2に示す組成のコーディエライト化原料及び造孔剤を用いたこと以外は、実施例1と同様にしてハニカム構造体（ハニカムフィルター）を得た。

【0074】

（評価結果）

表2、3に示すように造孔剤として発泡済みの発泡樹脂を、2～3.5質量部添加した実施例1～10のハニカム構造体では、隔壁の平均気孔径が、16.0～34.6μm、気孔率が55.5～72.0%であった。また、いずれの実施例でも、得られたハニカム構造体の気孔分布が、図4及び5に示すように、前記条件式（1）及び（3）の条件を満たしていた。また、比較的粗いタルク、シリカ原料を用いた実施例1及び7のハニカム構造体でも、これら関係式の条件を満たしており、発泡済みの発泡樹脂が成形直後に隔壁内で膨張するためと推察された。

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【0075】これに対し、造孔剤としてグラファイト、PET、及びPMMAを用いて製造した比較例1～4、6のハニカム構造体では、気孔が内部に偏在し、図4及び5に示すように、前記条件式（1）及び（3）のいずれの条件も満たさなかった。

【0076】このため、図5に示すように、各実施例のハニカム構造体では、各比較例の同程度の気孔率を有するハニカム構造体に比べ、一次成分振幅スペクトルと二次成分振幅スペクトルの平均値（X）が小さく、同気孔率のハニカム構造体の特性を比較すると、表3に示すように、各実施例のハニカム構造体の方が、各比較例のハニカム構造体よりも、捕集効率が高く、捕集圧損が低かった。また、図6に示すように、各ハニカム構造体を通じて、一次成分振幅スペクトルと二次成分振幅スペクトルの平均値（X）が小さい程、スト捕集圧損が小さくなる傾向が認められた。

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【0077】他方、非常に粗いシリカ原料を用いた比較例5のハニカム構造体では、シリカ粒子の一部が隔壁表面に現れて気孔を形成したため、前記条件式（1）の条件を満たしたが、平均気孔径が35μm以上であり、かつ前記条件式（3）の条件は満たさなかった。このため、このハニカム構造体では、捕集効率が65%と非常に低くなり、スト捕集圧損も非常に大きくなかった。

【0078】また、80℃以上で発泡する未発泡の発泡樹脂を用いて製造した比較例7のハニカム構造体では、前記条件式（1）及び（3）のいずれの条件も満たさず、しかも気孔率が44.4%と非常に低かったため、スト捕集圧損が非常に大きくなかった。これは、乾燥工程でバインダーのゲル化により成形体が硬化し、未発泡の発泡樹脂が成形体内で膨張するのを妨げられたためと考えられた。

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【0079】また、グラファイト10重量部と、発泡済みの発泡樹脂3.5重量部とを併用して製造した比較例8のハニカム構造体では、気孔率が75%以上となり、アイソスタティック強度が非常に小さくなつたため、スト捕集圧損の測定用治具にセットすることができなかつた。

【0080】

【表1】

	平均粒径(μm)
タルク A	20
タルク B	45
カオリン	10
アルミナ	5
水酸化アルミニウム	3
溶融シリカ A	25
溶融シリカ B	40
シリカ A	5
シリカ B	130
グラファイト	40
発泡済み発泡樹脂	50
未発泡発泡樹脂	15
PMMA	55
PET	50

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【0081】

【表2】

【表3】
【0082】

	コージェライト化原料配合割合(重量%)						造孔剤配合割合(重量%)				
	タルク	カオリン	アルミナ	水酸化アルミニウム	シリカ	溶融シリカ	グラファイト	泡沫樹脂	未発泡樹脂	PMMA	PET
実施例1	B:40	20	14	16		B:10		2			
実施例2	B:40	20	14	16		A:10		2			
実施例3	B:40	20	14	16		A:10		10	2		
実施例4	B:40	20	14	16	A:10			10	2		
実施例5	B:40	20	14	16		A:10			2		
実施例6	A:39	19	14.5	16.5	B:11						
実施例7	B:40	20	14	16							
実施例8	B:40	20	14	16							
実施例9	B:40	20	14	16							
実施例10	B:40	20	14	16							
実施例11	B:40	20	14	16							
比較例1	B:40	20	14	16		B:10		2			
比較例2	B:40	20	14	16		A:10		10	3		
比較例3	B:40	20	14	16		A:10		10	3		
比較例4	B:40	20	14	16		A:10		10	3		
比較例5	B:40	20	14	16	B:10						
比較例6	A:39	19	14.5	16.5	B:11						
比較例7	B:40	20	14	16		B:10					
比較例8	B:40	20	14	16	A:10						
比較例9	B:40	20	14	16		B:10		10	3		

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	気孔率 (%)	気孔径 (μm)	熱膨張係数 ($\times 10^{-4}/^\circ\text{C}$)	隔壁表面 層間長さ比	$L \times (0.3 \times \text{気孔率}/100) \times 0.91$	バージスペクトル 1,2次平均値 X	$X \times (-33 \times \text{気孔率}/100) \times 2.8$	捕集効率 (%)	捕集圧損 (kPa)	排ガス淨化効率 (%)
実施例 1	55.5	25.4	0.4	1.09	0.01	7.6	-2.1	90	9.8	9.8
実施例 2	55.7	20.4	0.4	1.09	0.01	7.2	-2.4	92	9.5	9.5
実施例 3	59.6	24.6	0.5	1.12	0.03	6.1	-2.2	80	8.9	8.9
実施例 4	60.5	16.0	0.4	1.10	0.01	4.1	-3.9	96	6.1	6.1
実施例 5	59.5	25.2	0.6	1.13	0.04	4.0	-4.4	90	8.0	8.0
実施例 6	59.1	34.6	0.7	1.14	0.05	7.7	-0.8	85	9.4	9.4
実施例 7	65.8	23.1	0.7	1.12	0.01	3.5	-2.8	91	7.1	7.1
実施例 8	65.8	23.9	0.8	1.13	0.02	3.1	-3.2	90	6.8	6.8
実施例 9	71.5	21.4	0.7	1.14	0.02	1.8	-2.6	93	6.2	6.2
実施例 10	72.0	21.8	0.8	1.15	0.02	1.5	-2.7	92	5.9	5.9
実施例 11								93		
比較例 1	55.6	25.3	0.4	1.08	-0.02	11.4	1.7	87	12.1	
比較例 2	59.4	21.7	0.5	1.07	-0.02	9.1	0.7	88	11.1	
比較例 3	65.1	22.4	0.7	1.09	-0.02	8.0	1.5	88	9.5	
比較例 4	70.9	22.6	0.8	1.09	-0.03	6.0	1.4	88	8.4	
比較例 5	58.0	39.2	1.1	1.13	0.05	13.7	4.8	65	12.1	
比較例 6	59.1	31.4	0.7	1.08	-0.01	11.8	3.3	79	11.4	
比較例 7	44.4	16.6	0.3	1.02	-0.02	14.1	0.8	97	13.1	
比較例 8	77.4	22.5	1.0	1.16	0.02	1.8	-0.7			
比較例 9								85		

※ 比較例 8 は強度が著しく弱いため、捕集効率、捕集圧損測定のための測定治具にセットできなかった。

【0083】

(実施例 11)

実施例 1において、貫通孔を目封じする工程を行わなかったこと以外は実施例 1と同様にしてサイズ：Φ 229.0 mm × L 152.0 mm、隔壁厚さ：300 μm 、セル密度：46.5 セル/ cm^2 のハニカム構造体（触媒担体）を製造した。

【0084】

(比較例 9)

実施例 1において、貫通孔を目封じする工程を行わなかったこと、及び表 1 及び表 2 に示す比較例 1 と同様の組成のコーディエライト化原料及び造孔剤を用いたこと以外は実施例

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1と同様にして、サイズ： $\phi 229.0\text{ mm} \times L 152.0\text{ mm}$ 、隔壁厚さ：300 μm 、セル密度：46.5セル/ cm^2 のハニカム構造体（触媒担体）を製造した。

【0085】

（評価結果）

得られた各ハニカム構造体に、高比表面積アルミナと白金系酸化触媒を500 g担持して触媒体としたところ、実施例11のハニカム構造体では、排ガス浄化効率が93%と大きかった。これに対して比較例9のハニカム構造体では、同様に高比表面積アルミナと白金系酸化触媒を500 g担持して触媒体としているにも拘わらず、排ガス浄化効率は85%と実施例11のハニカム構造体に比べ小さかった。

【0086】

【発明の効果】以上、本発明によれば、ストート等の捕集効率の向上、触媒の有効利用による浄化性能の向上、圧力損失の低減、及び捕集時間の長期化を効果的に達成することができ、延いてはフィルター再生時における溶損限界及びアイソスタティック強度を向上できる多孔質ハニカム構造体を提供することができる。このため、特に、ディーゼルパティキュレートフィルターや排ガス浄化用触媒担体等の排ガス浄化手段として好適である。

【図面の簡単な説明】

【図1】断層気孔率分布を測定する方法を示す隔壁の断面図である。

【図2】図1に示す方法により求めた断層気孔率分布の一例を示すグラフである。

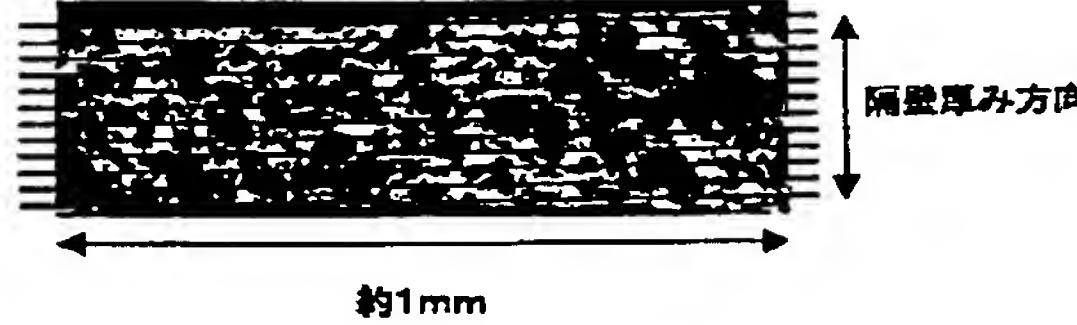
【図3】図2に示す断層気孔率分布を各級数でフーリエ変換した結果を示すグラフである。

【図4】各実施例及び比較例により、気孔率と展開長さ比との関係を示すグラフである。

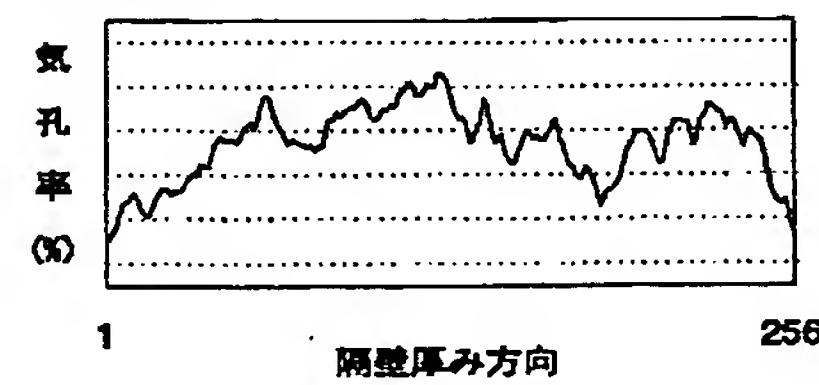
【図5】各実施例及び比較例により、気孔率と、一次成分振幅スペクトル（S）及び二次成分振幅スペクトル（F）の平均値（X）との関係を示すグラフである。

【図6】各実施例及び比較例により、一次成分振幅スペクトル（S）及び二次成分振幅スペクトル（F）の平均値（X）と、ストート捕集圧損との関係を示すグラフである。

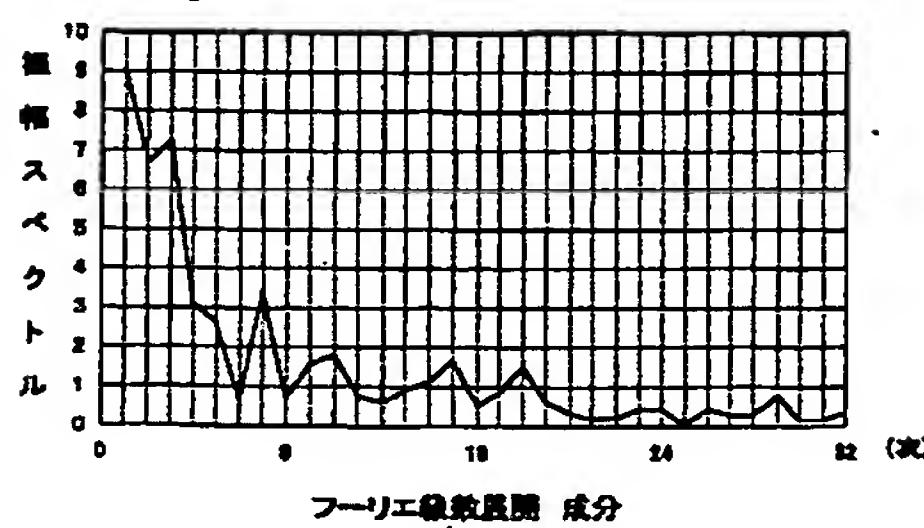
【図1】



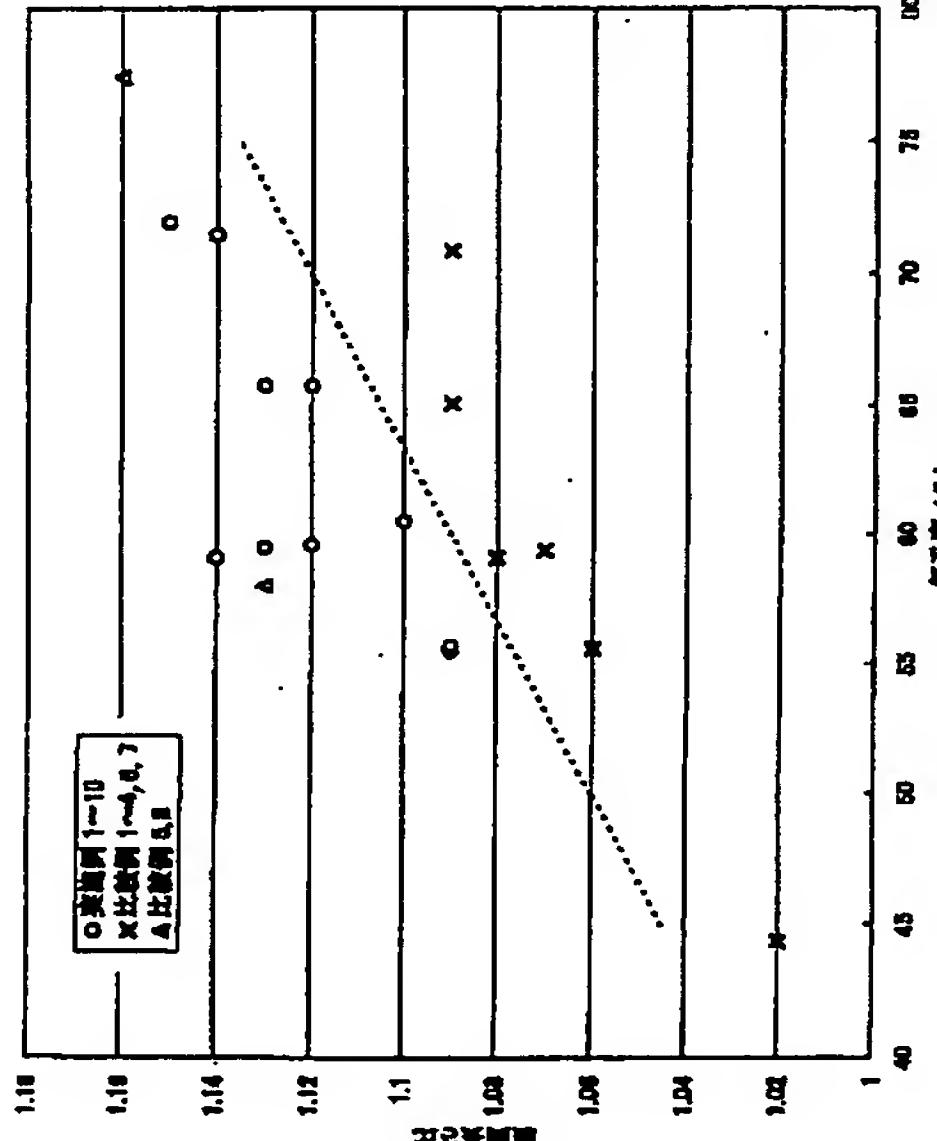
【図2】



【図3】



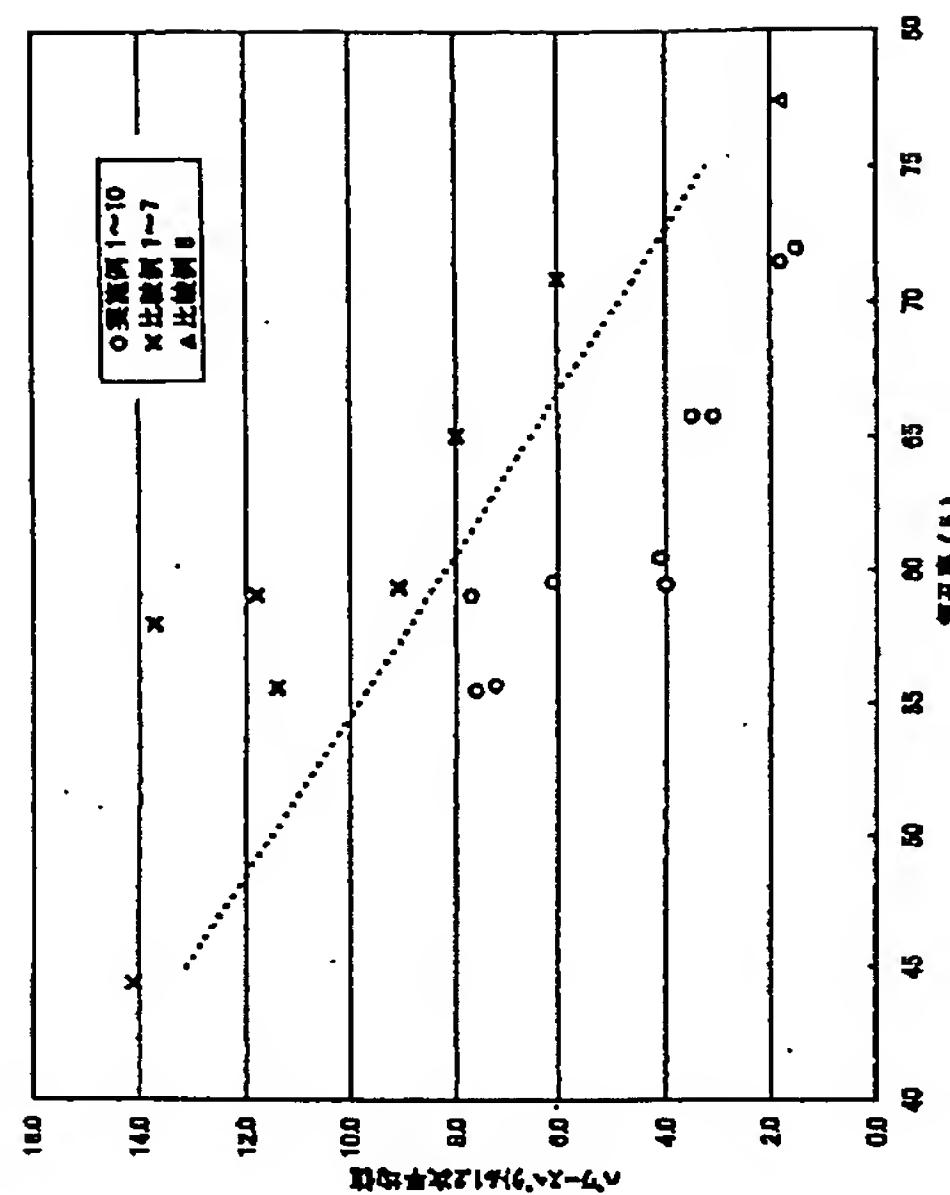
【図4】



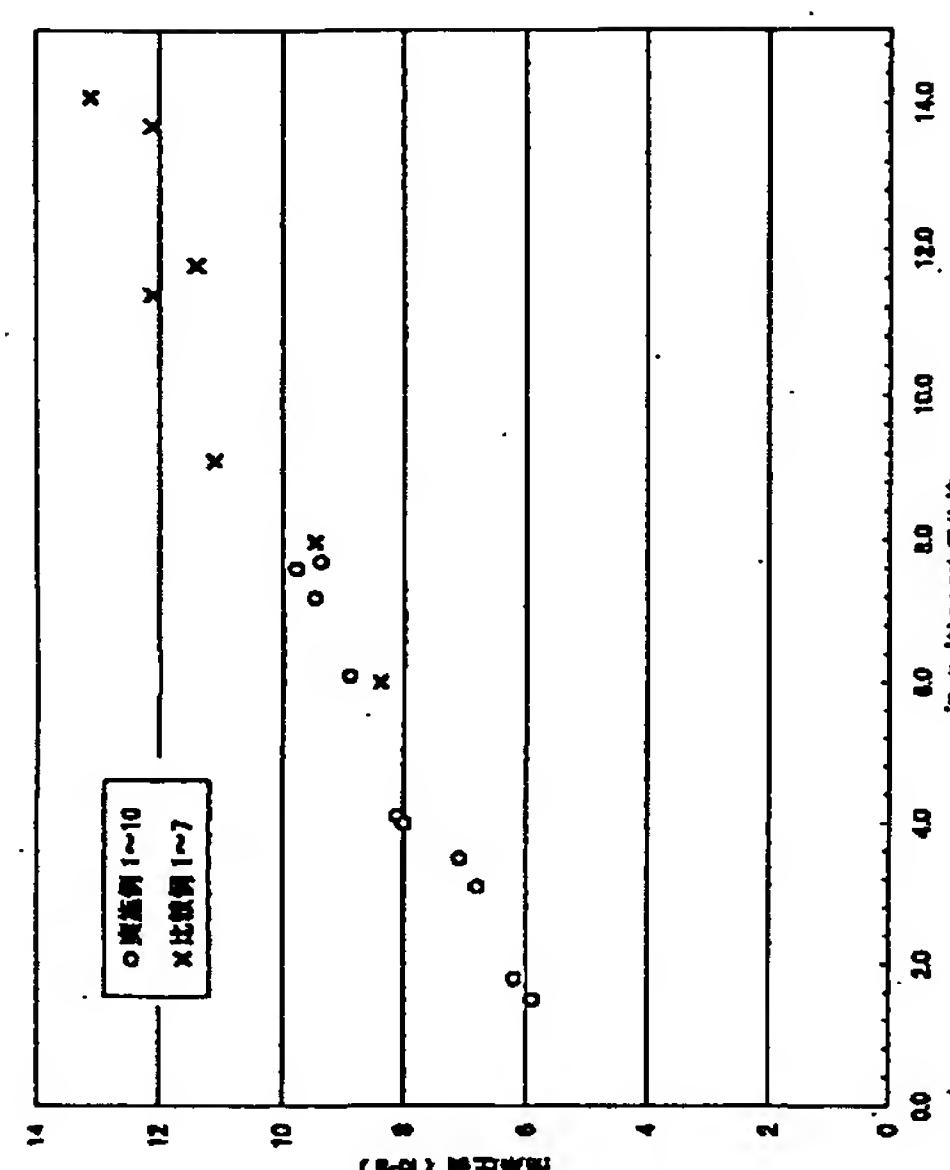
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【図 5】



【図 6】



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